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# Performance of Nitrogen as a Carrier Gas in Capillary Gas Chromatography Using a Thin Film Column

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# Performance of Nitrogen as a Carrier Gas in Capillary Gas Chromatography Using a Thin Film Column

By

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## APPROVAL FOR SUCCESSFUL DEFENSE

**Brittany A. Handzo** has successfully defended and made the required modifications to the text of the Master's Thesis for the **M.S.** during this **Fall Semester 2019.**

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The mentor and any other committee members who wish to review revisions will sign and date this document only when revisions have been completed. Please return this form to the Office of Graduate Studies in the College, where it will be placed in the candidate's file and submit a copy with your final dissertation to be bound as page number two.

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**Abstract**

Gas chromatography (GC) is one of the most widely used analytical techniques for the separation and analysis of volatile compounds. Solids, liquids, and gases, organic and inorganic materials, and large molecular weight compounds can all be analyzed via this technique. Gas chromatographic separations are fast, accurate, and reliable. One of the reasons why these separations are so efficient is because of the carrier gas. The purpose of the carrier gas is to carry the injected sample through the column. It is known as the mobile phase and does not interact chemically with the sample. Common carrier gases include helium, hydrogen, and nitrogen. Helium is the most frequently used, but increased demand has caused a worldwide helium shortage. This has forced scientists to look for alternative carrier gases and study how much they influence separation.

The purpose of this research is to explore the performance of nitrogen as an alternative GC carrier gas. Previous literature states that nitrogen is non-ideal because it yields long retention times due to the low optimum linear gas velocity and rapid band broadening. However, with nitrogen, it is also possible to generate the most efficient separations. Nitrogen is more cost-effective compared to helium. This research focuses on the comparison between nitrogen and helium carrier gases to determine whether nitrogen can be a replacement for helium. Compounds such as alkanes, essential oils, polycyclic aromatic hydrocarbons, and column test mixtures were all analyzed under temperature programmed conditions. Column performance calculations such as separation numbers, resolution, and efficiency were performed, and Van Deemter curves were created. Nitrogen proved effective and should be considered a reasonable alternative carrier gas in gas chromatography.

# 1.Introduction

## *1.1 Gas Chromatography*

Gas chromatography is one of the most commonly used analytical techniques for the separation and analysis of volatile compounds. Solids, liquids, and gases dissolved in volatile solvents can all be analyzed via this technique in addition to organic and inorganic materials. Gas chromatography can also analyze compounds with molecular weights ranging from 2 to over 1000 daltons.[1] As a result of the large variety of compounds that can be analyzed with this technique, gas chromatographs are the most widely used analytical instruments in the world.

There are many advantages of gas chromatography that contribute to its widespread usage in analytical laboratories. To begin, gas chromatography is fast and some analyses can be done within seconds. Chromatographers are always interested in fast methods and this is the fastest technique of them all. The analyses are also very efficient and sensitive. Studies are done with high resolution and with detection limits as low as parts per billion (ppb). Gas chromatography is nondestructive and can easily be coupled with a mass spectrometer.[1] Additionally, GC requires only a microliter sized sample. Overall, gas chromatography is accurate, reliable, simple, and relatively inexpensive.

## *1.2 Instrumentation*

Each part of a gas chromatograph plays a specific role in order to produce the most ideal conditions for separations to occur. The basic components of a typical gas chromatographic system are the carrier gas, flow control, inlet, sampling device, column, oven, detector, and data system. Each of these apparatuses contribute to how well the sample moves through the column and separates and how good the analysis will be. The instrumentation schematic is shown below.

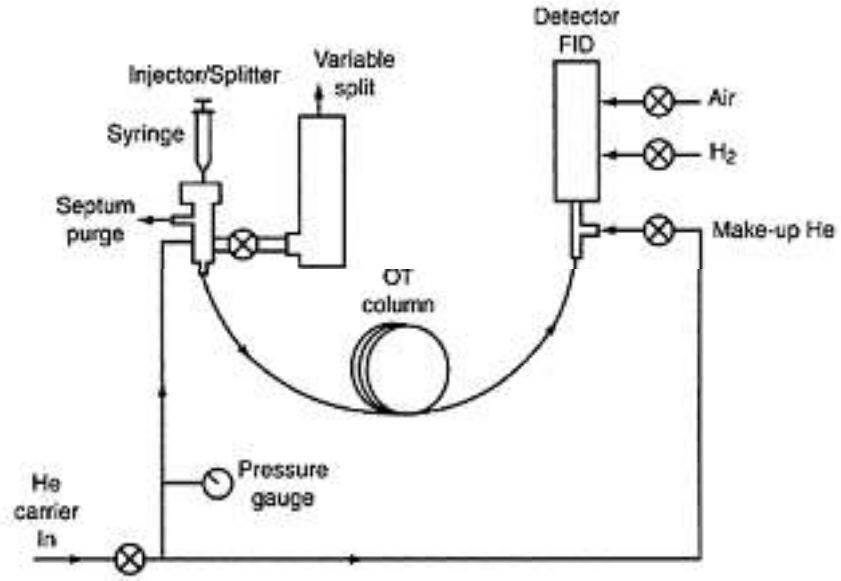


Figure 1: The diagram of a typical gas chromatograph.[1] The sample begins by being injected via syringe, moved by the carrier gas through the column, and is detected by an FID detector.

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The purpose of the carrier gas is to carry the injected sample through the column. It is known as the mobile phase and does not interact chemically with the sample. Common carrier gases include helium, hydrogen, nitrogen, and sometimes argon. Carrier gases will be discussed more thoroughly in the next section. Flow control allows for the measurement and regulation of the carrier gas.[1] These controls can alter the pressure of the carrier gas leaving the gas cylinder and entering the column. This is essential for determining the linear gas velocity needed for qualitative analysis.

Next, sample inlets and devices allow for the sample to be injected into the instrument. Inlets permit the samples to be rapidly and quantitatively introduced into the carrier gas stream. Sampling devices such as gas-sampling valves, syringes, septa, or auto-samplers allow the sample to physically be injected into the instrument.[1] Auto-samplers can handle more than 100 samples per day. Spilt and splitless controls dictate how much sample can enter the column. Most of these sampling devices can be controlled and changed directly from the software in the computer system.

Columns are the most important part of the chromatographic system. The column contains the stationary phase and is the location of analyte separation. Columns can be packed or capillary, but capillary columns are the most commonly used today. Packed columns are tubes filled with small grains of a solid or a high-melting liquid mixture that acts as the stationary phase. Capillary columns are much smaller and is usually made up of fused silica thinly coated inside the tube.[2] Efficient capillary columns can separate hundreds of components in samples such as complex natural products.[1] The oven is a temperature-controlled zone where the column is housed. The control of temperature is one of the most effective ways to influence separation.

Finally, the last parts of the instrument are the detectors and data systems. The detector senses the analytes from the column and provides a record of the chromatography that took place in a form of a chromatogram.[1] The signals are proportional to the quantity of analyte. Detectors can range from flame ionization (FID), thermal conductivity cell (TCD), or the electron capture (ECD). An FID detector was used in this research. Data systems are computers with software programs that are helpful in interpreting or integrating data. Just a few important jobs of software systems are the regulation of experimental conditions, control of auto-samplers, and data analysis.

### *1.3 Carrier Gases*

As stated before, the carrier gas is often referred to as the mobile phase and is responsible for transporting the analytes through the column. The carrier gas influences gas chromatographic separations mainly in two ways. First, the linear gas velocity of the carrier gas determines what speed the analytes will move through the column while they are in the gas phase. Linear velocity depends on the column dimensions, the pressure and temperature of the column, and the nature of the carrier gas.[3] In order to obtain a certain linear gas velocity, the viscosity of the carrier gas must be considered. Secondly, the diffusion of the analytes through the carrier gas affects peak broadening. The more peak broadening that occurs, the less efficient the separation. The less peak broadening, the more efficient the separation. These diffusion effects lead to the introduction of an optimum carrier gas velocity.[3] This optimum velocity is the point where the least peak broadening occurs and where separations will be the most effective. It is a balance between the diffusion rate and the carrier gas linear velocity.[3] Different carrier gases provide different optimal points. Overall, these are two of the main functions' carrier gases have that influence the performance of gas chromatographic separations.

### *1.3.1 Types of Carrier Gases*

The three most commonly used carrier gases in GC are helium, hydrogen, and nitrogen. Helium is the most popular choice in the United States for gas chromatographic applications. Its chemical properties such as low density and inertness make it an ideal and safe carrier gas. Helium yields very fast and efficient separations and is compatible with GC-MS systems. However, a global helium shortage is underway. In 1996, the Helium Privatization Act required the government to sell excess helium reserves at a very low flat rate.[4] Since helium was so inexpensive on the market, this resulted in wasteful usages of the gas in industry. After 18 years of overusing helium, the Helium Steward Act of 2012 allowed the cost of helium to rise to realistic market prices.[4] Since then, the already scarce and non-renewable carrier gas became more and more expensive. Today, many helium suppliers are rationing their helium supplies leaving many companies and universities without supplies. In addition, even businesses such as the Party City or Dollar Stores have increased the cost of balloons to keep up with the increasing cost of helium. This shortage is negatively impacting companies all across the world.

Because of this global helium shortage, alternative carrier gases have been explored. Hydrogen is the most commonly used carrier gas outside of the United States and is becoming more popular here since the helium crisis.[4] Hydrogen has great chromatographic properties such as fast analyses and efficient separations. Research shows that hydrogen can easily have faster analysis times compared to helium. Hydrogen can also operate at lower oven temperatures which can lead to longer column life. However, because hydrogen has a lower density and viscosity, almost every experimental condition needs to be adjusted. More importantly, hydrogen has much higher safety concerns compared to helium which often discourages many chromatographers from choosing it.

Nitrogen is another alternative carrier gas for helium. Nitrogen is a readily available and less expensive carrier gas that can be generated within a laboratory.[5] Nitrogen can yield the most efficient separations out of all three gases and is suitable for simple analyses. In addition, there are no safety concerns as with hydrogen. However, just like the other gases, there are some concerns. First, nitrogen is known to have slow analysis times and is not easily compatible with GC-MS.[5] Secondly, the Van Deemter curve, which will be explained later, shows that nitrogen has the lowest optimum linear velocity. However, scientists are still experimenting with nitrogen as a carrier gas in gas chromatographic applications. Some of these applications include detecting crude drugs in organic solvents, studying sulfur flame photometric detectors,[6] and determining diffusion coefficients.[7]

Nitrogen has been used as a gas chromatography carrier gas for years. In 1957, nitrogen gas was compared against other carrier gases to study retention times. Hydrogen was not included, but nitrogen was shown to have a shorter retention time then helium was methane was injected on a 10-foot charcoal column.[8] This was early evidence that, depending on experimental conditions, nitrogen can outperform helium. In 1967, nitrogen was used to study gas chromatographic separations in packed columns. The author, John Conder, noticed peak inversion with nitrogen and overcame this by reducing the gas flow rate.[9] Lowering the flow rate is still done today, with nitrogen having the best separations at lower velocities when compared to helium. In 1981, sulfur flame photometric detectors were explored using nitrogen as a carrier gas. The nitrogen gas was mixed with the detector flame air to, ideally, oxidize sulfur compounds.[10] This was another way that nitrogen carrier gas could positively influence gas chromatography.

In the end, each carrier gas has their own strengths and weaknesses. Helium is effective for all gas chromatography and GC-MS applications, but the global helium shortage has forced more research to be done with hydrogen and nitrogen as alternative GC carrier gases. This research will mainly focus on nitrogen and how this carrier gas compares with the very limited helium.

### *1.3.2 Viscosity of Carrier Gases*

Viscosity is one factor to be considered when choosing a GC carrier gas. The viscosity of a carrier gas determines the pressure drop required to obtain a certain linear gas velocity within a column. In addition to viscosity, this pressure drop is also dependent on the column length and diameter.[3] Gases that have higher viscosities will require a higher pressure drop to reach their optimum linear velocity and achieve the best separations. Gases that have lower viscosities will require a lower pressure drop to reach their optimum velocity. The viscosity is linearly related to the pressure drop so if the gas viscosity increases/decreases, the pressure drop will also increase/decrease.[3]

The chemical nature of carrier gases is important because each gas has a specific viscosity that can be susceptible to change. Shown in Figure 2, viscosity increases as temperature increases. Helium and nitrogen have similar viscosities, but they are extremely dependent on temperature. As the temperature increased, the viscosity changed and increased dramatically. Hydrogen has the lowest viscosity of all three gases. It was less susceptible to change as the temperature increased compared to helium and nitrogen. For experiments that rely heavily on temperature, hydrogen would be a good alternative carrier gas for helium.[3] For simple analyses, nitrogen is a good replacement for helium since they follow similar trends. In the end, carrier gas viscosity plays a role in the diffusion of analytes through the column, ultimately effecting the resolution and efficiency of gas chromatographic separations.

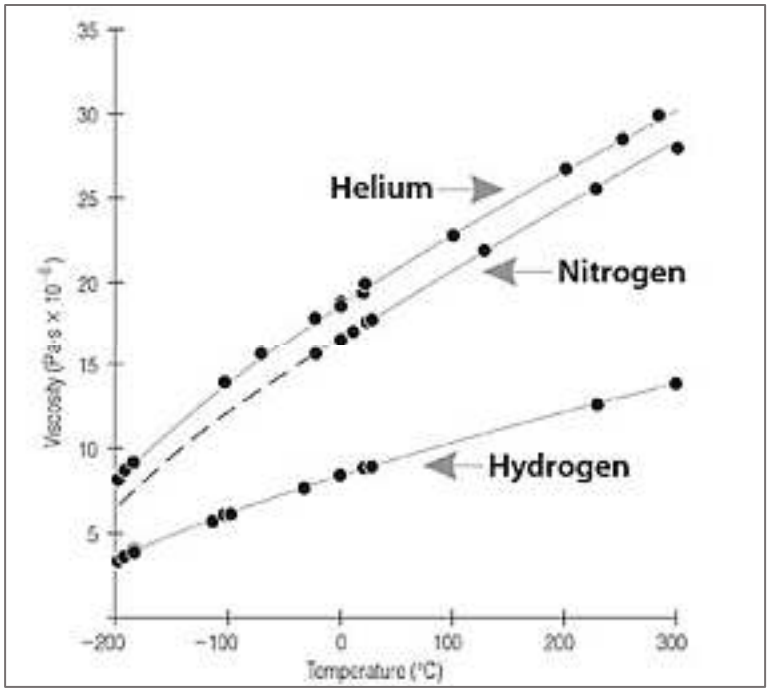


Figure 2: The relationship of three carrier gas viscosities to temperature.[3]

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### *1.3.3. Van Deemter Equation*

The Van Deemter equation is used to characterize the performance of a chromatographic column. It is also used to determine the optimum velocity of the carrier gas which is where the highest column efficiency will be. In isocratic conditions, the Van Deemter equation is written as:

$$(1)\quad H = A + B/\mu + C\mu$$

where H is the theoretical plate height, μ is the mobile phase linear velocity, and the A, B, and C terms are parameters that describe peak broadening.[11] The A term is eddy diffusion which accounts for the speed of the mobile phase flowing between different channels of a packed column. The B term is longitudinal diffusion which refers to the diffusion of molecules from the sample in the mobile phase and along the longitudinal direction of the column. Lastly, the C term accounts for the mass transfer of the sample between the stationary and mobile phases to ensure that a dynamic equilibrium is met.[11] All three of these parameters are the main sources of peak broadening.[12] The Van Deemter equation was later updated to account for the narrower peaks produced from capillary separations and was named the Golay equation. Capillary columns do not contain any packaging material so there is no influence on peak broadening from the A term, eddy diffusion. Therefore, the A term is removed. The Golay equation is commonly written as:

$$(2)\ H = B/\mu + C_S\mu + C_M\mu$$

where the variables are defined the same as in the Van Deemter equation, H being plate height, μ being the mobile phase linear velocity, B as longitudinal diffusion, and C as mass transfer. $C_S$ is the mass transfer for the analyte in or on the stationary phase where $C_M$ is the mass transfer in the mobile phase. Van Deemter curves are created by plotting the theoretical plate height (H) by the column efficiency (N).[13] H is defined as the column length divided by the column efficiency. It is sometimes referred to as the height equivalent to the theoretical plate or HETP. μ is defined as the

column length divided by the retention time of an unretained compound ($t_m$). Every carrier gas will have a different Van Deemter curve and comparison of these graphs can help understand which carrier gas will be the most effective. Carrier gases at the lowest minimum plate height tend to give the most efficient separations. This means that each gas will have an optimum at a different linear velocity. Shown in Figure 3 is the Van Deemter curve for the three carrier gases of helium, hydrogen, and nitrogen. Hydrogen has an optimum between 30-50 cm/sec, helium has an optimum between 20-40 cm/sec, and nitrogen has an optimum between 10-20 cm/sec.[11]

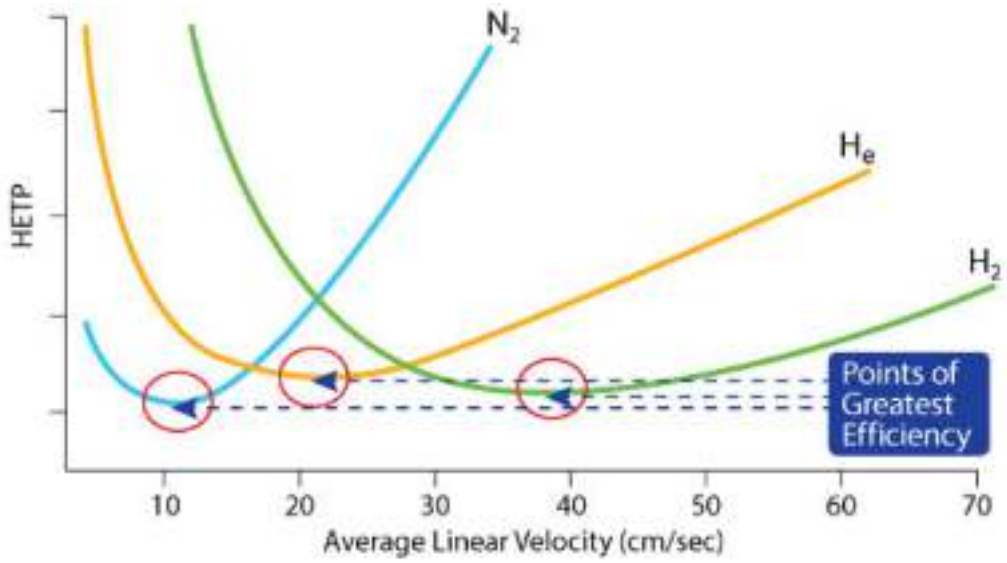


Figure 3: Van Deemter curves for the three carrier gases of helium, nitrogen, and hydrogen.[5]

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The Van Deemter curve in Figure 3 shows that nitrogen has the lowest minimum plate height, meaning it has the highest efficiency compared to helium and hydrogen. However, nitrogen also has a much steeper curve and a much narrower velocity range. Even though nitrogen is an effective gas, the efficiency decreases at higher flow rates.[13] This is because at higher velocities, the B term of the Golay equation, or longitudinal diffusion, gets smaller. This can limit the operating conditions to lower flow rates for nitrogen. Helium has a much flatter curve compared to nitrogen which is ideal when choosing a carrier gas. The flatter curve shows that the efficiency of separations is not decreased when the linear velocity is changed. The analysis time of helium is also shorter since the velocity of the carrier gases can be increased.[15] Finally, hydrogen has the highest optimum linear velocity and flattest Van Deemter curve of all three gases. This means that it is actually the fastest carrier gas and has the shortest analysis times. The flattest of all three curves, hydrogen has good efficiency over a wide range of linear velocities which makes it a good choice for samples that elute over a long range of temperatures.[15] Gradual slopes are more desirable because there is a smaller efficiency loss as the flow rate increases. Overall, the Van Deemter curve and equation gives very useful information about which carrier gas will perform the best for specific gas chromatographic applications.

### *1.3.4 Which Gas Should You Choose?*

Because carrier gases are such a key element in gas chromatographic separations, choosing the right carrier gas can play a huge role on how effective your analysis will be. As stated before, helium is the most ideal since it is fast, efficient, and safe but a global shortage has made helium hard to obtain. Alternatives to helium have focused mainly on hydrogen since Van Deemter curves suggest the gas is the fastest and very efficient. However, nitrogen is also a reasonable alternative

because it yields very good efficiencies and is extremely cost effective for laboratories. The purpose of this research is to explore the performance of nitrogen as a carrier gas under isothermal and temperature programmed conditions for a variety of applications. The objective is to determine whether nitrogen can be a reasonable alternative for the replacement of helium in gas chromatography.

### *1.4 Column Performance*

There are several measures used to evaluate column performance in GC. Under isothermal conditions, parameters such as resolution and plate number are calculated to determine how well the instrument performed. Resolution is a measure of relative separation of chromatographic peaks. Plate number is an index that describes the overall effectiveness and efficiency of a capillary column. Under temperature programming conditions, separation numbers are used to calculate the overall performance. Separation numbers are the number of peaks that can be resolved between two adjacent peaks. All of these terms were chosen for this research because it was important to have numerical values that would describe the performance of the chromatographic separations. These terms were also useful when comparing the separations between the two carrier gases. These terms will be explained more in the next sections.

#### *1.4.1 Separation Numbers*

In gas chromatography, a separation number (SN) is defined as the number of peaks that can be resolved between two consecutive *n*-alkane peaks with $z$ and ($z$ +1) carbon atoms.[14] The general formula for a separation number is:

$$(3) \quad SN = \frac{t_{R(z+1)} - t_{Rz}}{w_{h(z+1)} + w_{hz}} - 1$$

The separation number depends on the analyte used for the analysis so they must be specified with any SN value. The variables include $t_R$ and $w_h$ which are retention time of two consecutive alkanes and peak width of two consecutive alkanes respectively. Retention time is a key variable for separation number and is defined as

$$(4) \quad t_R = t'_R + t_M$$

where $t'_R$ is the adjusted retention time and $t_M$ is the gas hold-up time.[17] The SN can be calculated in any part of a chromatogram and it was throughout this research.

### *1.4.2 Plate Height*

In general, plate height is defined as

$$(5) \quad H = L/N$$

where L is the column length and N is the number of theoretical plates.[1] In isothermal chromatography, plate height, H, is constant at any point along the column. It is expressed in Equation 6 below. In temperature programming chromatography, H varies from point to point along the column and is expressed in Equation 7.

$$(6) \quad H = L(\tau/t)^2$$

$$(7) \quad H = L(\tau/t_R)^2$$

In both cases, the variables are defined the same where $\tau$ is the standard deviation, t is the time to the peak, and L is the column length.[18] Therefore, plate height follows the same fundamental ideas for both temperature programming chromatography and isothermal chromatography. Plate height was calculated isothermally in this research.

### *1.4.3 Resolution and Efficiency*

One way to measure the efficiency and selectivity of a column is resolution. Resolution expresses the degree in which adjacent peaks are separated, or the measure of relative separation of chromatographic peaks.[19] The formula is

$$(8) \quad R = \Delta t_r / 0.5(w_1 + w_2)$$

where $\Delta t_r$ is the difference in retention times of the adjacent peaks and w are the widths of the adjacent peaks.[1] The larger the value, the better the separation. Baseline separation requires a resolution value of 1.5.[1] According to Fryer, resolution can be improved by increasing the length of the column provided that the flow rate is also increased.[19]

Furthermore, another way to measure the efficiency of a chromatographic system is the plate number (N). N is one index used to determine the overall effectiveness and performance of a capillary column.[20] It is defined as

$$(9) \quad N = 16(t_r/w)^2$$

where $t_r$ is the retention time and w is the peak width.[1] A large N value states that the column is acting efficiently which is desirable for good separations. Since retention times and peak widths are measured directly from the chromatogram, N is unitless.[1] In a practical gas chromatographic analyses, it is ideal to operate the column for high efficiency in addition to other factors such as minimum analysis times, narrow peak shapes, and sensitivity.[21] In the end, resolution and plate number are two parameters used to study column performance and overall column separation.

### *1.4.4 The Grob Test Mixture*

The Grob test mixture is a standard test mixture used to test the performance of a capillary column. This test demonstrates the absence of secondary interactions and assesses the silanol activity of the column wall.[22] It can help explain peak deformation, adverse adsorption effects, or stationary phase coating effects. The Grob test mixture can also indicate acid-base characteristics on the column.[22] Each component in the mixture has a specific function that states what an absence or presence of a peak means. Table 1 summarizes the probe compounds and their functions.

| The Grob Test Mixture Components | |
|---|---|
| **Probe Compounds** | **Function** |
| n-alkanes | column efficiency |
| fatty acid methyl esters | separation number, column efficiency |
| 1-octanol | detection of hydrogen-bonding sites, silanol groups |
| 2,3-butanediol | silanol group detection |
| 2-octanone | detection of activity associated with Lewis acids |
| nonanal | aldehyde adsorption other than via hydrogen bonding |
| 2,6-dimethylphenol | acid-base character |
| 2,6-dimethylaniline | acid-base character |
| 4-chlorophenol | acid-base character |
| n-decylamine | acid-base character |
| 2-ethylhexanoic acid | irreversible adsorption |
| dicyclohexylamine | irreversible adsorption |

Table 1: The Grob test mixture probe compounds and their respective functions.[23]

### *1.5 Optimum Separation Conditions*

Optimum conditions are needed in gas chromatography in order to produce the most ideal results. Shorter retention times, or volumes, and lesser peak broadening have always been of interest to chromatographers. A lot of theoretical work has been completed to determine which physical parameters are most important when trying to separate adjacent peaks. This is directly related to the determination of optimal operating conditions for the separation of analytes in gas chromatography.

There are many principles applied when finding optimum conditions for capillary columns. According to Giddings,[24] if the retentive process is pure partition, the plate height is written as:

$$(10) \quad H=B/\upsilon +C\upsilon + E\upsilon$$

where υ are the local gas velocities, B is longitudinal diffusion, C is the square of the liquid layer thickness, and E is tube radius squared. A variety of variables can then be optimized by only considering H such as flow velocity and pressure. These factors do not influence the H factor and therefore can be improved. For the flow velocity, the value of υ is shown in Equation 11 while the optimal value for the plate height is shown in Equation 12.

$$(11) \quad \upsilon =[B/(C+E)]^{1/2}$$

$$(12) \quad H=2[B(C+E)]^{2}$$

The variables are defined the same as above. Since the pressure over a wide range is inversely proportional to the gaseous diffusion coefficient, the equation is rewritten in as:

$$(13) \quad H=B'/p\upsilon + C\upsilon +E'p\upsilon$$

In Equation 13, all the variables are defined the same with the addition of p, pressure.

At the optimum velocity, the final equation is shown in Equation 14 below. Similar optimum conditions can be found for variables such as tube diameter, film thickness, and temperature.

$$(14) \quad H=[(B'/p)(C+E'p)]^2$$

Another variable used for optimization in the past has been the separation function, F. According to Giddings,[24] F has been found to be an acceptable measure of the extent of separation. It is not as common nowadays, but it can still give valuable information about basic chromatography. It is defined in Equation 15 below as:

$$(15) \quad F = \frac{L\left(\frac{1}{R_I}-\frac{1}{R_{II}}\right)^2}{8\left(\frac{H_I}{R_I{}^2}+\frac{H_{II}}{R_{II}{}^2}\right)}$$

where resolution, plate height, and column length are all considered. The term "separation per unit time" is defined by dividing F by column length.[24] Practically, since F is proportional to column length, this term gives a relative separability for columns of equal length. It allows us to define chromatography between different columns.

### *1.5.1 Temperature Programming*

One of the most commonly used experimental techniques in gas chromatography is temperature programed gas chromatography (TPGC). TPGC is different from isothermal techniques because the temperature is increased as the chromatographic run progresses. The temperature rise is linear in time and is represented by the equation:

$$(16) \quad T-T_o=\beta t$$

where T is the temperature, $T_o$ is the beginning temperature, and β is the heating rate in °C per unit time, t.[25] The initial temperature can be set to any degree lower or greater than room temperature and then increased through TPGC up to 300-500°C depending on the instrument. TPGC has the

ability to separate mixtures with a wide range of boiling points. This is extremely difficult in isothermal analyses since the isothermal temperature is always too high or too low for some components in the mixture. In this research, the 15-component mixture, the Grob test mixture, the essential oils, and the PAH mixture were all run under TPGC.

Peak migration through the column as the temperature increases in TPGC can be shown in Figure 4. The exponential curve represents the relative migration rate, which is related to the vapor pressure. It is approximated that the acceleration of the sample moves faster than the vapor pressure.[26] This is because the carrier gas expands as the temperature increases and pressure decreases as it moves towards the outlet. To sum up, as the column temperature increases, the carrier gas expands inside the column as it flows from the inlet to outlet which results in the peak accelerating simultaneously along the column.[26] This entire phenomenon, approximated by Giddings, is known as the "step approximation" model and can be seen in Figure 4.

Unlike isothermal experiments, the components in a sample move slowly at first and then accelerate exponentially as the temperature increases. The combination of increased vapor pressure and acceleration due to gas expansion yields shorter retention times and sharper peaks. However, carrier gas viscosity also causes the flow to decrease as temperature increases. Nitrogen is assumed to be a bad carrier gas choice under isothermal conditions due to band broadening. Yet, the step function and acceleration of peaks under TPGC limits that band broadening. This should lessen the broadening effect previously predicted by the Van Deemter plots.

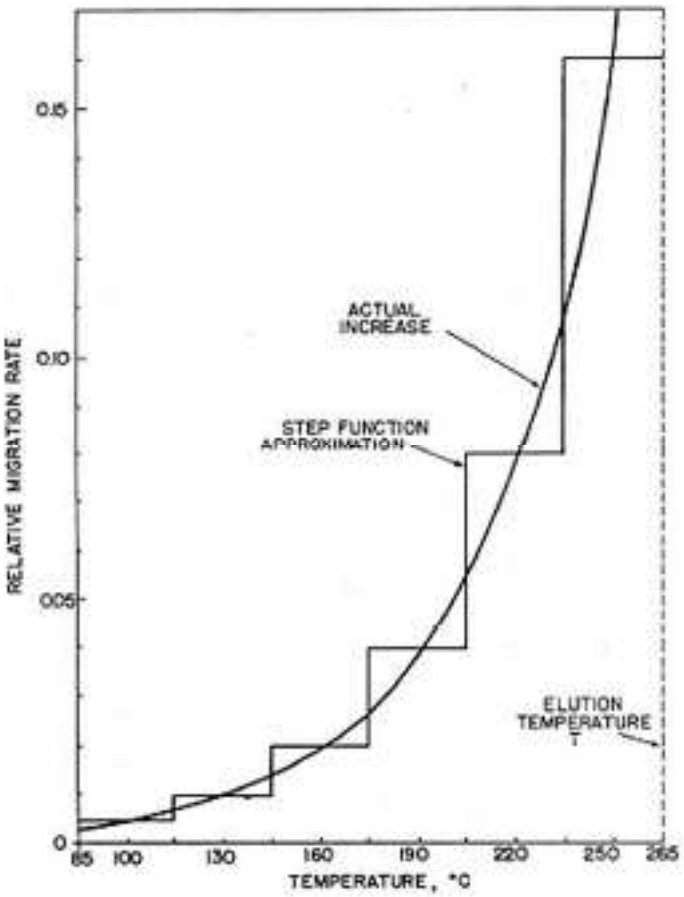


Figure 4: The step function approximation for the rate of zone migration in TPGC.[15]

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There are many advantages to using temperature programming conditions when compared to isothermal conditions. First, TPGC is known to produce sharper and narrower peaks unlike the broader and shorter peaks in isothermal trials. This is based on the acceleration of the rate along the column as the temperature program increases.[26] Since peak widths are used for fundamental calculations such as efficiency, resolution, or separation number, narrower peaks in TPGC will provide more ideal data when compared to isothermal conditions. Another pro of TPGC is that it can reveal peaks with broad, low shapes that may have been missed if the experiment was ran isothermally.[27] Lastly TPGC experiments have shorter retention times because of the fast elution of the analytes which is always beneficial in both industry and academia.

### *1.6 Mixtures Used in this Work*

There was a variety of compounds chosen for this research in order to test the performance of different carrier gases over a large range of gas chromatographic applications. The four groups of chemicals tested in this research were alkanes, the Grob test mixture components, polycyclic aromatic hydrocarbons (PAHs), and essential oils. These all have applications in different areas of science such as biology, chemistry, environmental studies, the flavor and fragrance industries, and many more.

Alkanes are acyclic saturated hydrocarbons. Alkanes are used in many branches of chemistry including gas chromatography. Since alkanes are very simple compounds, they are often used to study GC fundamentals and optimization methods for the instrument. They are also used as a basis for retention index systems[28] and for studies comparing linear relationships between the number of carbon atoms in a chain to the partition coefficient. Similarly, linear relationship studies

comparing retention times and number of carbon atoms in temperature programming experiments are often done. Finally, alkanes allow for the usage of the separation number calculation to evaluate carrier gas performance.

The Grob test mixture was another mixture used in this research. This mixture is a simple way to check column performance and ensure everything is working before conducting any thorough studies.[29] The Grob's text mixture is commonly used in the gas chromatography industry with companies such as Restek, Phenomenex, and Sigma-Aldrich all supplying this mixture to customers. The Grob test mixture has also been updated many times and has influenced many other programmed test mixtures to be published for capillary columns.

Another group of chemicals tested in this research were polycyclic aromatic hydrocarbons. A polycyclic aromatic hydrocarbon (PAH) is an organic compound containing carbon and hydrogen arranged into multiple aromatic rings. These are a class of chemicals that are naturally occurring in coal, gasoline, and crude oil. They can also be produced when tobacco, wood, garbage, gasoline, oil, or coal are burned.[30] Naphthalene is a common PAH that is commercially produced to make a variety of chemicals and other products, most famously mothballs. Unfortunately, PAHs can bind or even form small particles in the air causing many health and environmental issues.[30] Lastly, since PAH's are analytes with wide boiling point ranges, they have been used in many gas chromatographic applications. Agilent developed a GC/GC-MS method for analyzing PAH's found in pumpkin seed oil [31] and Restek was able to develop and use a GC method to detect PAH's in Yerba Mate Tea, [32] a tea commonly found with high levels of PAHs in Brazil.

The last group of compounds explored in this work were essential oils. Essential oils are natural, volatile oils obtained from plants or other natural sources. These oils are extracted by distillation methods with the goal of obtaining their characteristic scents. These scents are then used in a variety of industries such as aromatherapies, fragrances, and flavors to create products such as perfumes. Essential oils have also been found to have healing properties. For example, bergamot has been used to improve skin conditions like eczema, sandalwood is used to calm nerves, and lavender is used to reduce stress. The essential oils tested in this research were peppermint oil, lavender oil, eucalyptus oil, and patchouli oil. These were complex mixtures with closely eluting peaks.

## 2. Experimental Procedure

### *2.1 Instrumentation*

All experimentation was performed on a Shimadzu Nexis-2030 gas chromatograph (Columbia, MF) equipped with a flame ionization detector (FID), split/splitless inlet, and an AOC Series Shimadzu auto-sampler. The inlet and detector were set at 250°C. A Shimadzu capillary column with the dimensions of 30 m by 0.25 mmID by 0.25 µm film thickness and a stationary phase of 5% phenyl polydimethylsiloxane was used. Helium and nitrogen (Airgas) were alternated as the carrier gases. The data acquisition program was Lab Solutions Lite by Shimadzu.

### *2.2 Alkane Analysis*

The fifteen alkanes of hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane, and eicosane ($C_6$-$C_{20}$) were used for the analysis. A 10 µL sample of each alkane was dissolved in 10 mL of hexane,

placed into an autosampler vial, and capped. All alkanes were purchased from Sigma-Aldrich (Milwaukee, WI). A 1 µL sample of this mixture was injected via autosampler. The inlet and detector were set to 250°C, temperature programming range was 70-250°C, split ratio was 50:1, pressure was 20 psi, and the temperature programming rates were 3, 5, 8, 10, 13, 15, and 20°C/min.

A second alkane analysis was done using tetradecane ($C_{14}$). A 100 µL sample of $C_{14}$ was dissolved in hexane and injected via autosampler. The same instrumentation, column, carrier gases, and software system were used. However, the experimental conditions were changed. The experiment was run isothermally at 180°C with varying pressures of 30, 40, 50, 60, 70 80, and 90 psi. The inlet and detector were set to 250°C and the split ratio was 20:1.

### *2.3 The Grob Test Mixture Analysis*

A programmed test mixture dissolved in dichloromethane (the Grob test mixture) purchased from Millipore Sigma (Bellefonte PA) was used for this analysis. This mixture contained the thirteen probe components of 2,3-butanediol, n-decane, n-undecane, 1-octanol, 2-ethylhexanoic acid, nonyl aldehyde, 2,6-dimethylphenol, 2,6-dimethylaniline, methyl decanoate, methyl undecanoate, dicyclohexylamine, methyl laurate, and an internal standard.[22] A 1 µL sample of the Grob test mixture was injected via autosampler. The same instrumentation, column, carrier gases, and software system was used. The inlet was set to 250°C while the detector was set to 300°C. The temperature programming range was 50-200°C with a rate of 10°C/min. This was held for an additional 3 minutes to ensure all components were eluted. Split ratios of 50:1 and 15:1 were tried.

### *2.4 Essential Oil Analysis*

Four essential oils (peppermint oil, lavender oil, eucalyptus oil, and patchouli oil) by Aura Cacia (Norway, IA) purchased from a local Target were tested. A 1 mL sample of each oil was dissolved in 10 mL of dichloromethane to create four separate solutions. The same instrumentation, column, carrier gases, and software system was used. The inlet was set to 200°C while the detector was set to 280°C. The column was held at 45°C for 2 minutes and then a rate of 10°C/min was used until 130°C was reached. A second temperature programming rate was applied at 30°C/min until 280°C was reached. The head pressure was 20 psi with a split of 120:1.

### *2.5 PAH Analysis*

A 16-component PAH mixture (610 PAH Calibration Mix B) was purchased from Restek (Bellefonte, PA) This mixture contained: naphthalene, acenaphthylene, fluorene, acenaphthene, phenanthrene, anthracene, fluoranthene, benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, pyrene, chrysene, and indeno(1,2,3-CD)pyrene. A 1 µL sample of the PAHs were injected via autosampler. The same instrumentation, column, carrier gases, and software system was used. The inlet was set to 250°C while the detector was set to 330°C. The temperature was held at 100°C for 1 minute and then a rate of 5°C/min was used until 330°C was reached. The oven was held for an additional 5 minutes to ensure all the components were eluted. Splitless injections were set.

## 3. Results and Discussion

### *3.1 $C_6$-$C_{20}$ Alkane Analysis*

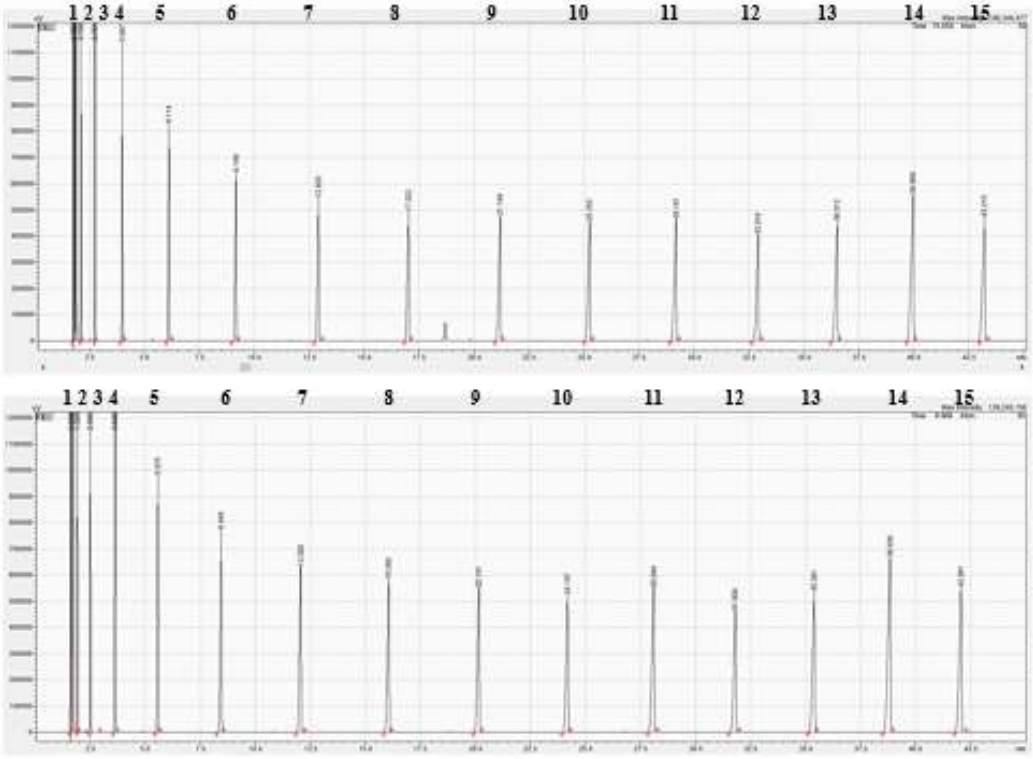
The following data describes the separations of the fifteen alkanes ($C_6$-$C_{20}$) under two different carrier gases, helium and nitrogen. The mixture was run under the temperature programming rates of 3, 5, 8, 10, 13, 15, and 20°C/min under helium and then nitrogen. The experiment was repeated in triplicate to ensure reproducibility and standard deviations were found. The chromatograms between the two carrier gases were compared and separation numbers were calculated.

#### *3.1.1 Helium and Nitrogen Chromatographic Separations*

Helium is the most commonly used carrier gas, known to give fast and efficient separations. Nitrogen is a less common carrier gas in gas chromatography. This is mainly because literature suggests nitrogen gives slow analyses and cannot operate at the fast linear velocities of helium and hydrogen. However, with the ongoing helium shortage, nitrogen was explored as an alternative carrier gas for helium. Show below are the separations of the 15-alkane mixture with both gases.

Figure 5 shows two separations of alkanes using helium and nitrogen carrier gases with a temperature programming rate of 3°C/min. Figure 5A shows the 15 alkanes eluting under helium gas while Figure 5B shows the same 15 alkanes eluting under nitrogen gas. As shown by the data above, the separations were very similar chromatographically and numerically for both gases. Total analysis time averaged around 43 minutes with nitrogen having a slightly lower analysis time. There were no major peak deformities such as fronting or tailing for any separation. Furthermore, the peak shapes were also very similar. Peaks that were more intense with helium as the carrier gas were also intense with nitrogen as the mobile phase. The separation numbers both increased until the tenth carbon, which decreased because the earlier carbons elute off the column quickly.

# Figure 5: Alkane Separations @ 3°C/min



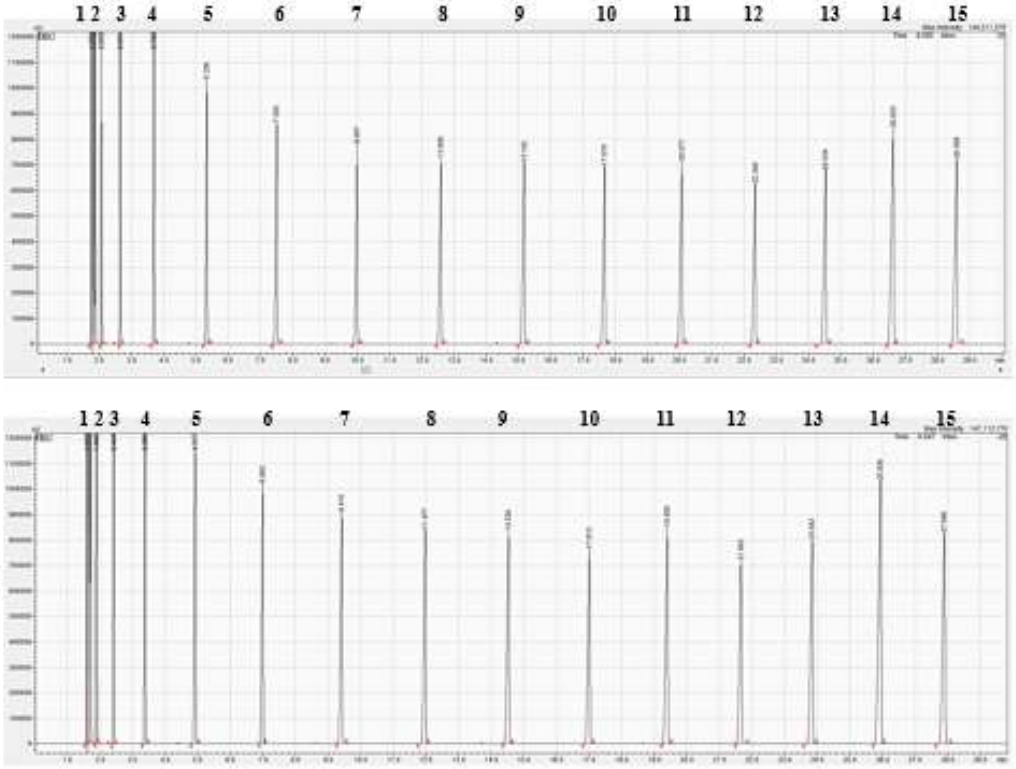

| Carbon # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| $C_{20}$-$C_{19}$ | 12.6 | 12.1 | 1-hexane |
| $C_{19}$-$C_{18}$ | 14.1 | 13.1 | 2-heptane |
| $C_{18}$-$C_{17}$ | 16.2 | 14.8 | 3-octane |
| $C_{17}$-$C_{16}$ | 17.0 | 15.9 | 4-nonane |
| $C_{16}$-$C_{15}$ | 18.9 | 17.5 | 5-decane |
| $C_{15}$-$C_{14}$ | 20.5 | 18.8 | 6-undecane |
| $C_{14}$-$C_{13}$ | 22.0 | 20.3 | 7-dodecane |
| $C_{13}$-$C_{12}$ | 24.3 | 21.9 | 8-tridecane |
| $C_{12}$-$C_{11}$ | 26.0 | 22.9 | 9-tetradecane |
| $C_{11}$-$C_{10}$ | 26.5 | 23.2 | 10-pentadecane |
| $C_{10}$-$C_{9}$ | 25.8 | 21.4 | 11-hexadecane |
| $C_{9}$-$C_{8}$ | 21.3 | 15.8 | 12-heptadecane |
| $C_{8}$-$C_{7}$ | 13.4 | 8.26 | 13-octadecane |
| $C_{7}$-$C_{6}$ | 6.42 | 3.66 | 14-nonadecane |
| SN: unitless | | | 15-eicosane |

Figure 5: Alkane separation under helium (5A) and nitrogen (5B) carrier gases with respective separation numbers from 3°C/min temperature programming conditions.

Figure 6 shows two separations of alkanes using helium and nitrogen carrier gases with a temperature programming rate of 5°C/min. Figure 6A shows the 15 alkanes eluting under helium gas while Figure 6B shows the same 15 alkanes eluting under nitrogen gas. As shown by the data above, the separations were again extremely similar for both carrier gases. Both total analysis times averaged around 28 minutes with nitrogen having a slightly lower retention time. There were no major peak deformities such as fronting or tailing for any separation. Furthermore, separation numbers were again similar and had the same decreasing trend at the tenth carbon. The separation numbers decreased overall with an increased rate of 5°C/min because the analytes are eluting so quickly that the efficiency is slightly lowered. In the end, the 5°C/min temperature programming rate also produced nearly identical results despite switching the carrier gases each trial.

Figure 7 shows two separations of alkanes using helium and nitrogen carrier gases with a temperature programming rate of 8°C/min. Figure 7A shows the 15 alkanes eluting under helium gas while Figure 7B shows the same 15 alkanes eluting under nitrogen gas. The data once again shows that the separations were extremely similar both chromatographically and numerically. Both total analysis times averaged around 20 minutes with nitrogen having a slightly lower retention time. There were no major peak deformities such as fronting or tailing and the peak shapes were again similar. The separation numbers were comparable and slightly lower with an increasing temperature rate. These values prove that nitrogen separated the alkanes just as efficiently as helium. In the end, the 8°C/min temperature programming rate also produced nearly identical results with no carrier gas outperforming the other.

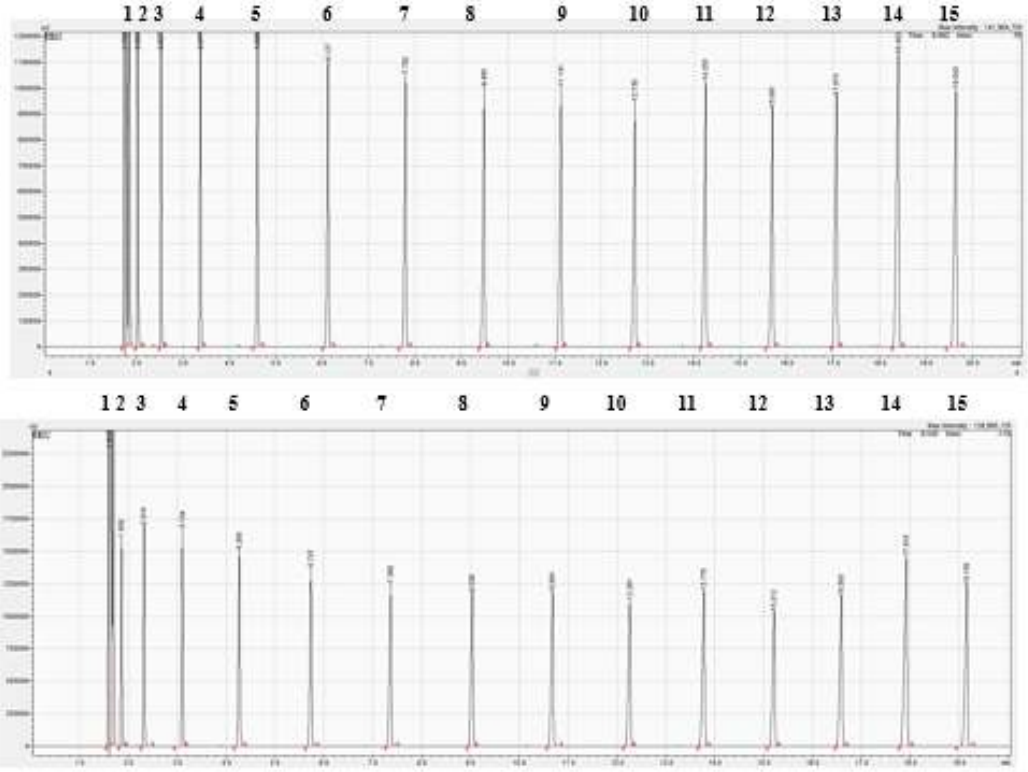
# Figure 6: Alkane Separations @ 5°C/min




| Carbon # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| $C_{20}$-$C_{19}$ | 11.6 | 11.0 | 1-hexane |
| $C_{19}$-$C_{18}$ | 12.5 | 12.0 | 2-heptane |
| $C_{18}$-$C_{17}$ | 14.5 | 14.0 | 3-octane |
| $C_{17}$-$C_{16}$ | 15.7 | 14.8 | 4-nonane |
| $C_{16}$-$C_{15}$ | 17.5 | 16.0 | 5-decane |
| $C_{15}$-$C_{14}$ | 19.5 | 17.8 | 6-undecane |
| $C_{14}$-$C_{13}$ | 20.3 | 19.1 | 7-dodecane |
| $C_{13}$-$C_{12}$ | 22.2 | 20.3 | 8-tridecane |
| $C_{12}$-$C_{11}$ | 23.9 | 21.2 | 9-tetradecane |
| $C_{11}$-$C_{10}$ | 24.5 | 21.5 | 10-pentadecane |
| $C_{10}$-$C_{9}$ | 23.8 | 20.0 | 11-hexadecane |
| $C_{9}$-$C_{8}$ | 19.2 | 15.0 | 12-heptadecane |
| $C_{8}$-$C_{7}$ | 12.2 | 8.28 | 13-octadecane |
| $C_{7}$-$C_{6}$ | 5.93 | 3.61 | 14-nonadecane |
| SN: unitless | | | 15-eicosane |

Figure 6: Alkane separation under helium (6A) and nitrogen (6B) carrier gases with respective separation numbers from 5°C/min temperature programming conditions.

# Figure 7: Alkane Separations @ 8°C/min



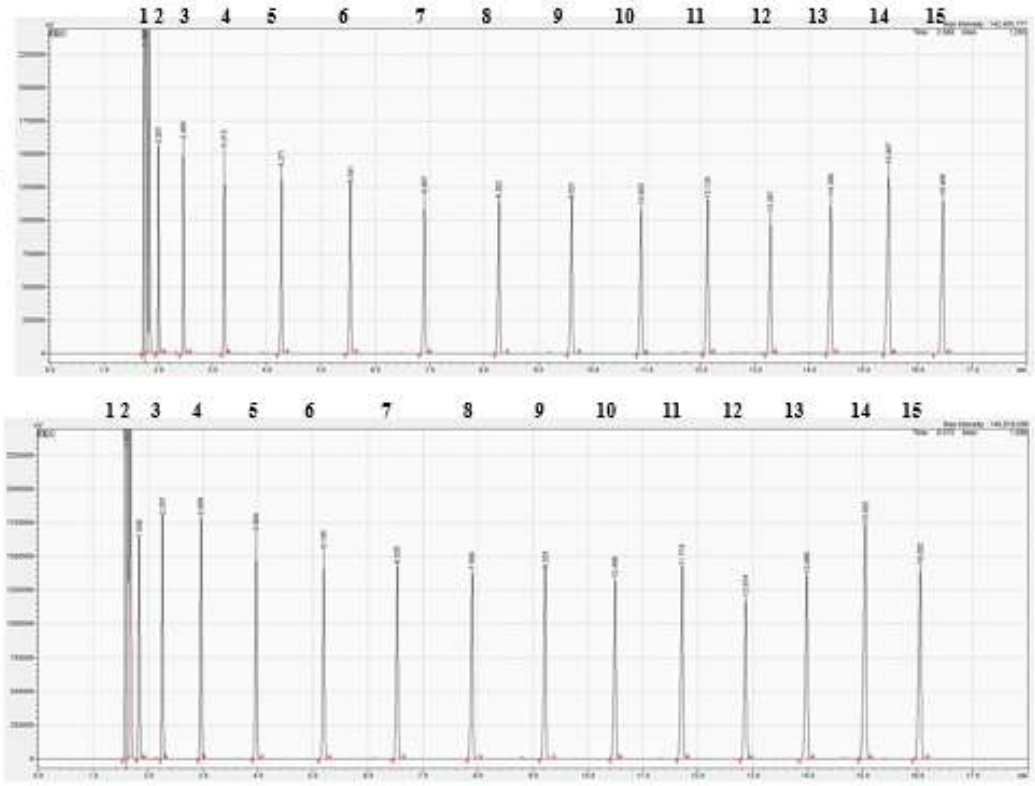

| Carbon # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| $C_{20}$-$C_{19}$ | 10.1 | 9.88 | 1-hexane |
| $C_{19}$-$C_{18}$ | 11.3 | 10.6 | 2-heptane |
| $C_{18}$-$C_{17}$ | 13.3 | 12.3 | 3-octane |
| $C_{17}$-$C_{16}$ | 14.2 | 13.2 | 4-nonane |
| $C_{16}$-$C_{15}$ | 15.2 | 14.3 | 5-decane |
| $C_{15}$-$C_{14}$ | 16.7 | 15.5 | 6-undecane |
| $C_{14}$-$C_{13}$ | 18.3 | 16.3 | 7-dodecane |
| $C_{13}$-$C_{12}$ | 19.7 | 17.6 | 8-tridecane |
| $C_{12}$-$C_{11}$ | 20.6 | 19.1 | 9-tetradecane |
| $C_{11}$-$C_{10}$ | 21.4 | 19.4 | 10-pentadecane |
| $C_{10}$-$C_{9}$ | 20.6 | 17.5 | 11-hexadecane |
| $C_{9}$-$C_{8}$ | 16.7 | 13.0 | 12-heptadecane |
| $C_{8}$-$C_{7}$ | 10.7 | 7.20 | 13-octadecane |
| $C_{7}$-$C_{6}$ | 5.00 | 3.15 | 14-nonadecane |
| SN: unitless | | | 15-eicosane |

Figure 7: Alkane separation under helium (7A) and nitrogen (7B) carrier gases with respective separation numbers from 8°C/min temperature programming conditions.

Figure 8 shows two separations of alkanes using helium and nitrogen carrier gases with a temperature programming rate of 10°C/min. Figure 8A shows the 15 alkanes eluting under helium gas while Figure 8B shows the same 15 alkanes eluting under nitrogen gas. The data once again shows that the separations were extremely similar for both carrier gases. Both total analysis times averaged around 16 minutes with nitrogen having a slightly lower total analysis time. The same trends as the previous experiments, no peak deformities, comparable separation numbers, and similar peak shapes, were again seen. Helium had slightly higher values when compared to nitrogen, but this was very minimal. Similar values were seen when the experiment, for all rates, were repeated two additional times. See *Appendix* section for those separation numbers. In the end, the 10°C/min temperature programming rate produced ideal results for both carrier gases.

Figure 9 shows two separations of alkanes using helium and nitrogen carrier gases with a temperature programming rate of 13°C/min. Figure 9A shows the 15 alkanes eluting under helium gas while Figure 9B shows the same 15 alkanes eluting under nitrogen gas. The data once again shows that the separations were extremely similar for both carrier gases. Both retention times averaged around 13 minutes with nitrogen having a slightly lower retention time. The same trends as the previous trials such as no peak deformities, close separation numbers, and similar peak shapes were again observed even with an increased rate of ten times what was originally analyzed. In the end, the 13°C/min temperature programming rate produced nearly identical results for both helium and nitrogen carrier gases.

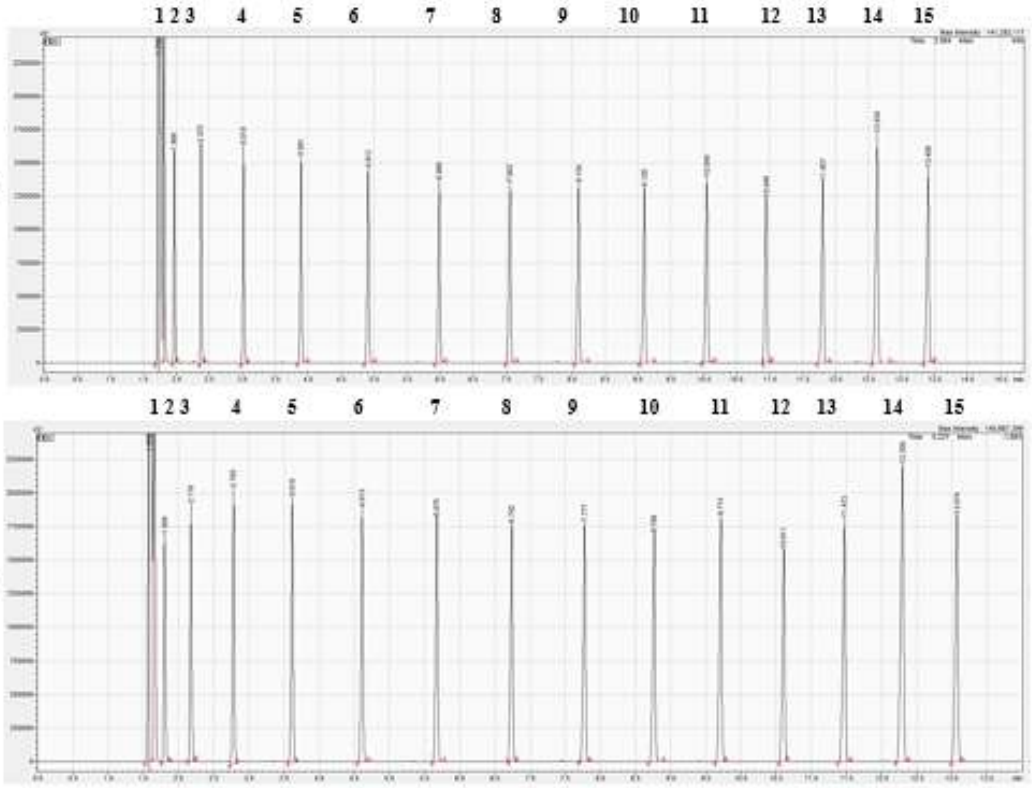
# Figure 8: Alkane Separations @ 10°C/min




| Carbon # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| $C_{20}$-$C_{19}$ | 9.63 | 9.42 | 1-hexane |
| $C_{19}$-$C_{18}$ | 10.7 | 10.2 | 2-heptane |
| $C_{18}$-$C_{17}$ | 12.4 | 11.4 | 3-octane |
| $C_{17}$-$C_{16}$ | 13.1 | 12.3 | 4-nonane |
| $C_{16}$-$C_{15}$ | 14.3 | 13.7 | 5-decane |
| $C_{15}$-$C_{14}$ | 16.0 | 14.9 | 6-undecane |
| $C_{14}$-$C_{13}$ | 17.3 | 15.8 | 7-dodecane |
| $C_{13}$-$C_{12}$ | 18.6 | 16.9 | 8-tridecane |
| $C_{12}$-$C_{11}$ | 20.0 | 17.8 | 9-tetradecane |
| $C_{11}$-$C_{10}$ | 20.5 | 18.2 | 10-pentadecane |
| $C_{10}$-$C_{9}$ | 19.7 | 16.6 | 11-hexadecane |
| $C_{9}$-$C_{8}$ | 16.1 | 12.5 | 12-heptadecane |
| $C_{8}$-$C_{7}$ | 9.93 | 6.94 | 13-octadecane |
| $C_{7}$-$C_{6}$ | 4.67 | 2.97 | 14-nonadecane |
| SN: unitless | | | 15-eicosane |

Figure 8: Alkane separation under helium (8A) and nitrogen (8B) carrier gases with respective separation numbers from 10°C/min temperature programming conditions.

# Figure 9: Alkane Separations @ 13°C/min



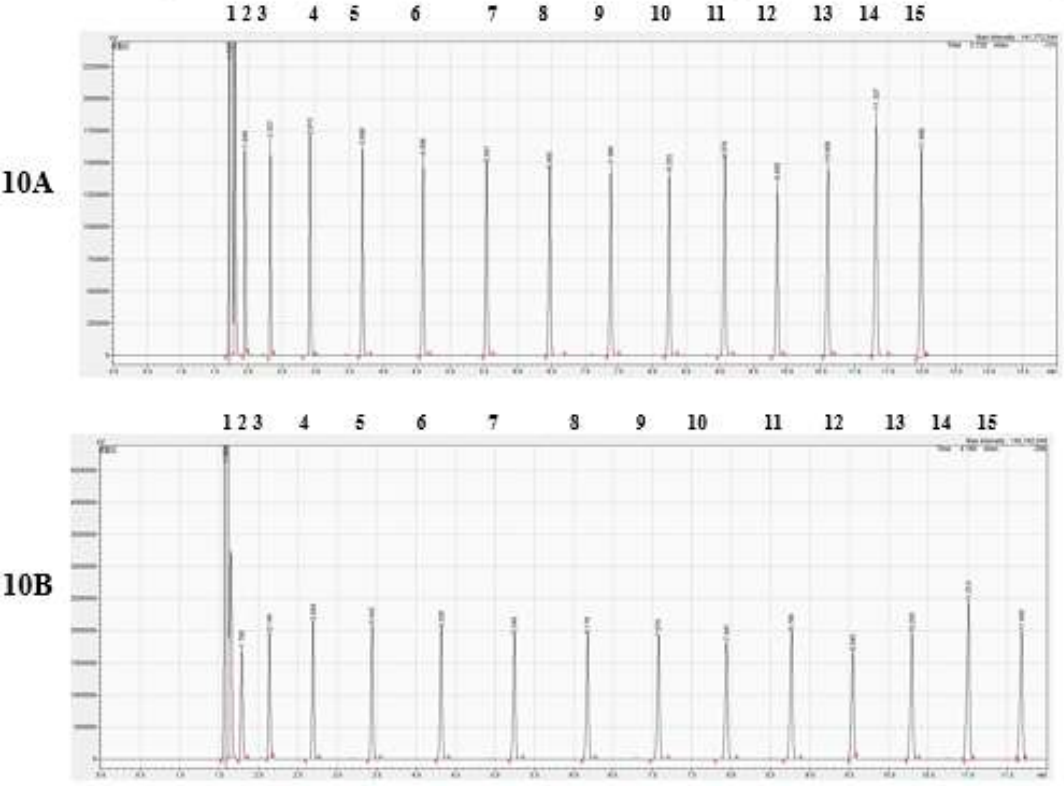

| Carbon # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| $C_{20}$-$C_{19}$ | 9.03 | 8.33 | 1-hexane |
| $C_{19}$-$C_{18}$ | 9.74 | 9.07 | 2-heptane |
| $C_{18}$-$C_{17}$ | 11.3 | 10.3 | 3-octane |
| $C_{17}$-$C_{16}$ | 12.2 | 11.3 | 4-nonane |
| $C_{16}$-$C_{15}$ | 13.0 | 12.2 | 5-decane |
| $C_{15}$-$C_{14}$ | 14.3 | 13.1 | 6-undecane |
| $C_{14}$-$C_{13}$ | 15.5 | 14.2 | 7-dodecane |
| $C_{13}$-$C_{12}$ | 16.6 | 15.4 | 8-tridecane |
| $C_{12}$-$C_{11}$ | 17.6 | 16.1 | 9-tetradecane |
| $C_{11}$-$C_{10}$ | 18.3 | 16.1 | 10-pentadecane |
| $C_{10}$-$C_{9}$ | 17.2 | 14.7 | 11-hexadecane |
| $C_{9}$-$C_{8}$ | 13.6 | 12.9 | 12-heptadecane |
| $C_{8}$-$C_{7}$ | 8.93 | 5.84 | 13-octadecane |
| $C_{7}$-$C_{6}$ | 4.30 | 2.60 | 14-nonadecane |
| SN: unitless | | | 15-eicosane |

Figure 9: Alkane separation under helium (9A) and nitrogen (9B) carrier gases with respective separation numbers from 13°C/min temperature programming condition

Figure 10 shows two separations of alkanes using helium and nitrogen carrier gases with a temperature programming rate of 15°C/min. Figure 10A shows the 15 alkanes eluting under helium gas while Figure 10B shows the same 15 alkanes eluting under nitrogen gas. The data once again shows that the separations were extremely similar for both carrier gases. With almost identical values for each of the seven chosen rates, this is another reason why nitrogen should be considered a reasonable alternative for helium for alkane separations. Both analysis times averaged around 11 minutes with nitrogen having a slightly lower analysis time. The same trends as the previous experiments, no peak deformities, similar separation numbers, and parallel peak shapes were again seen. In the end, the 15°C/min temperature programming rate produced nearly identical results to prove that these two carrier gases behave similarly when separating alkanes.

Finally, Figure 11 shows two separations of alkanes using helium and nitrogen carrier gases with a temperature programming rate of 20°C/min. Figure 11A shows the 15 alkanes eluting with helium gas while Figure 11B shows the same 15 alkanes eluting with nitrogen gas. The data once again shows that the separations were extremely similar for both carrier gases. Both analysis times averaged around 9 minutes with nitrogen having a slightly lower analysis time. By increasing the temperature programming rate from 3°C/min to 20°C/min the alkanes eluted in less than 10 minutes. This is ideal for fast separations in both the industrial and academic fields. Likewise, the same trends were observed again, no peak deformities, close separation numbers, and similar peak shapes. In the end, the 20°C/min temperature programming rate proved that helium and nitrogen perform in a similar manner when analyzing and separating alkane mixtures.

# Figure 10: Alkane Separations @ 15°C/min

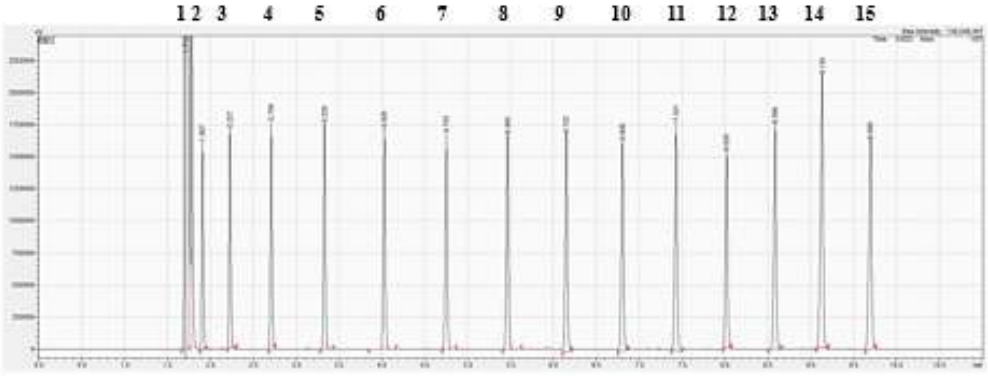



| Carbon # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| $C_{20}$-$C_{19}$ | 8.60 | 7.86 | 1-hexane |
| $C_{19}$-$C_{18}$ | 9.57 | 8.85 | 2-heptane |
| $C_{18}$-$C_{17}$ | 11.1 | 10.4 | 3-octane |
| $C_{17}$-$C_{16}$ | 11.6 | 10.8 | 4-nonane |
| $C_{16}$-$C_{15}$ | 12.1 | 11.5 | 5-decane |
| $C_{15}$-$C_{14}$ | 13.2 | 12.5 | 6-undecane |
| $C_{14}$-$C_{13}$ | 14.6 | 13.3 | 7-dodecane |
| $C_{13}$-$C_{12}$ | 16.1 | 14.5 | 8-tridecane |
| $C_{12}$-$C_{11}$ | 16.5 | 15.3 | 9-tetradecane |
| $C_{11}$-$C_{10}$ | 16.7 | 15.2 | 10-pentadecane |
| $C_{10}$-$C_{9}$ | 16.4 | 1.0 | 11-hexadecane |
| $C_{9}$-$C_{8}$ | 13.3 | 10.5 | 12-heptadecane |
| $C_{8}$-$C_{7}$ | 8.45 | 7.75 | 13-octadecane |
| $C_{7}$-$C_{6}$ | 4.05 | 2.53 | 14-nonadecane |
| SN: unitless | | | 15-eicosane |

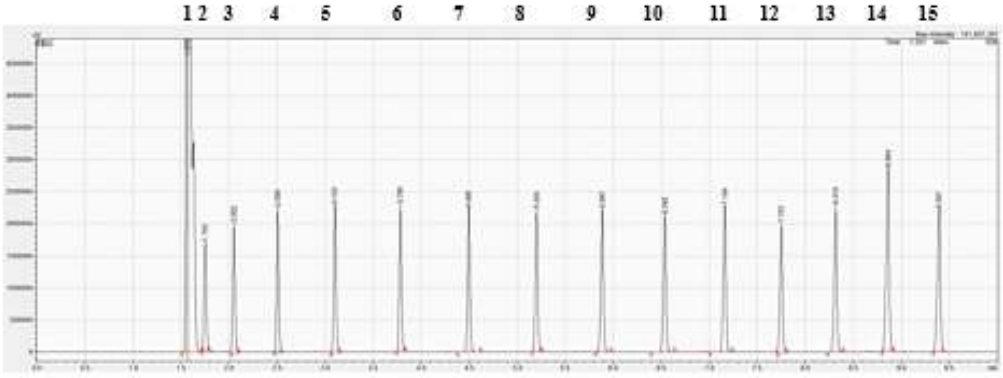
Figure 10: Alkane separation under helium (10A) and nitrogen (10B) carrier gases with respective separation numbers from 15°C/min temperature programming conditions.

# Figure 11: Alkane Separations @ 20°C/min

11A




11B




| Carbon # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| $C_{20}$-$C_{19}$ | 7.58 | 7.33 | 1-hexane |
| $C_{19}$-$C_{18}$ | 7.98 | 7.93 | 2-heptane |
| $C_{18}$-$C_{17}$ | 9.27 | 8.93 | 3-octane |
| $C_{17}$-$C_{16}$ | 9.73 | 9.33 | 4-nonane |
| $C_{16}$-$C_{15}$ | 10.6 | 10.1 | 5-decane |
| $C_{15}$-$C_{14}$ | 11.4 | 11.1 | 6-undecane |
| $C_{14}$-$C_{13}$ | 12.2 | 11.9 | 7-dodecane |
| $C_{13}$-$C_{12}$ | 13.3 | 12.6 | 8-tridecane |
| $C_{12}$-$C_{11}$ | 13.7 | 13.0 | 9-tetradecane |
| $C_{11}$-$C_{10}$ | 14.2 | 12.9 | 10-pentadecane |
| $C_{10}$-$C_{9}$ | 13.8 | 11.7 | 11-hexadecane |
| $C_{9}$-$C_{8}$ | 11.1 | 8.70 | 12-heptadecane |
| $C_{8}$-$C_{7}$ | 6.80 | 4.75 | 13-octadecane |
| $C_{7}$-$C_{6}$ | 3.24 | 2.10 | 14-nonadecane |
| SN: unitless | | | 15-eicosane |

Figure 11: Alkane separation under helium (11A) and nitrogen (11B) carrier gases with respective separation numbers from 20°C/min temperature programming conditions.

In the end, helium produced very fast and efficient separations as the literature suggested. However, nitrogen produced even faster separations which was not expected but can be beneficial. The nitrogen alkane separations were almost identical to the helium alkane separations in terms of peak shapes, retention times, and separation numbers. In both cases, all 15 alkanes were eluted cleanly and quickly with efficient separations. This experiment was also run in triplicate, as shown in the appendix, with similar results. Overall, helium is a favorable carrier gas choice, but nitrogen is also an excellent option that should be considered as an alternative GC carrier gas.

### *3.1.2 Standard Deviations*

Standard deviations are useful to ensure that experiments are reproducible. With triplicate testing done at seven different temperature programming rates (21 trials per carrier gas), it was important to calculate the standard deviations for the retention times of the $C_6$-$C_{20}$ alkanes. The tables below show the statistics for both helium and nitrogen.

The tables below represent the standard deviations for the peak retention times for three rounds of alkane trials. The variability between retention times were minimal with the highest value being only 0.468. The slower temperature programming rates had higher deviations when compared to the faster temperature programming rates. This is because the separations took much longer and there is a higher chance of peak broadening as the sample moves through the column. The usage of an auto-sampler on the Nexis-2030 gas chromatograph contributed to the low standard deviations and is much better for reproducibility compared to manual injections. Overall, the standard deviations were very small, proving that the experiment is reproducible.

| Table 2: $t_R$ Standard Deviations for Rate 3°C/min | | |
|---|---|---|
| Alkane | Helium SD | Nitrogen SD |
| Eicosane | 0.218 | 0.066 |
| Nonadecane | 0.266 | 0.107 |
| Octadecane | 0.468 | 0.125 |
| Heptadecane | 0.374 | 0.031 |
| Hexadecane | 0.146 | 0.263 |
| Pentadecane | 0.372 | 0.384 |
| Tetradecane | 0.193 | 0.290 |
| Tridecane | 0.300 | 0.222 |
| Dodecane | 0.354 | 0.205 |
| Undecane | 0.054 | 0.014 |
| Decane | 0.040 | 0.123 |
| Nonane | 0.019 | 0.032 |
| Octane | 0.132 | 0.246 |
| Heptane | 0.080 | 0.091 |
| SD=unitless | | |

Table 2: Standard Deviations for the retention times of the triplicate alkane testing at 3°C/min.

| Table 3: $t_R$ Standard Deviations for Rate 5°C/min | | |
|---|---|---|
| Alkane | Helium SD | Nitrogen SD |
| Eicosane | 0.261 | 0.090 |
| Nonadecane | 0.250 | 0.104 |
| Octadecane | 0.446 | 0.163 |
| Heptadecane | 0.118 | 0.102 |
| Hexadecane | 0.137 | 0.096 |
| Pentadecane | 0.285 | 0.341 |
| Tetradecane | 0.344 | 0.253 |
| Tridecane | 0.163 | 0.216 |
| Dodecane | 0.349 | 0.163 |
| Undecane | 0.378 | 0.005 |
| Decane | 0.191 | 0.005 |
| Nonane | 0.189 | 0.000 |
| Octane | 0.000 | 0.085 |
| Heptane | 0.075 | 0.075 |
| SD=unitless | | |

Table 3: Standard Deviations for the retention times of the triplicate alkane testing at 5°C/min.

| **Table 4: $t_R$ Standard Deviations for Rate 8°C/min** | | |
|---|---|---|
| Alkane | Helium SD | Nitrogen SD |
| Eicosane | 0.129 | 0.111 |
| Nonadecane | 0.176 | 0.156 |
| Octadecane | 0.188 | 0.177 |
| Heptadecane | 0.416 | 0.073 |
| Hexadecane | 0.228 | 0.066 |
| Pentadecane | 0.252 | 0.083 |
| Tetradecane | 0.283 | 0.235 |
| Tridecane | 0.208 | 0.260 |
| Dodecane | 0.130 | 0.121 |
| Undecane | 0.158 | 0.127 |
| Decane | 0.172 | 0.245 |
| Nonane | 0.311 | 0.116 |
| Octane | 0.132 | 0.064 |
| Heptane | 0.075 | 0.054 |
| SD=unitless | | |

Table 4: Standard Deviations for the retention times of the triplicate alkane testing at 8°C/min.

| Table 5: $t_R$ Standard Deviations for Rate 10°C/min | | |
|---|---|---|
| Alkane | Helium SD | Nitrogen SD |
| Eicosane | 0.142 | 0.141 |
| Nonadecane | 0.061 | 0.016 |
| Octadecane | 0.208 | 0.193 |
| Heptadecane | 0.298 | 0.073 |
| Hexadecane | 0.235 | 0.208 |
| Pentadecane | 0.214 | 0.159 |
| Tetradecane | 0.231 | 0.099 |
| Tridecane | 0.255 | 0.008 |
| Dodecane | 0.261 | 0.009 |
| Undecane | 0.172 | 0.134 |
| Decane | 0.193 | 0.146 |
| Nonane | 0.179 | 0.118 |
| Octane | 0.000 | 0.143 |
| Heptane | 0.014 | 0.170 |
| SD=unitless | | |

Table 5: Standard Deviations for the retention times of the triplicate alkane testing at 10°C/min.

| Table 6: $t_R$ Standard Deviations for Rate 13°C/min | | |
|---|---|---|
| Alkane | Helium SD | Nitrogen SD |
| Eicosane | 0.066 | 0.052 |
| Nonadecane | 0.068 | 0.114 |
| Octadecane | 0.085 | 0.187 |
| Heptadecane | 0.094 | 0.083 |
| Hexadecane | 0.196 | 0.090 |
| Pentadecane | 0.116 | 0.106 |
| Tetradecane | 0.118 | 0.123 |
| Tridecane | 0.137 | 0.130 |
| Dodecane | 0.000 | 0.126 |
| Undecane | 0.174 | 0.119 |
| Decane | 0.174 | 0.118 |
| Nonane | 0.009 | 0.109 |
| Octane | 0.113 | 0.121 |
| Heptane | 0.061 | 0.037 |
| SD=unitless | | |

Table 6: Standard Deviations for the retention times of the triplicate alkane testing at 13°C/min.

| Table 7: $t_R$ Standard Deviations for Rate 15°C/min | | |
|---|---|---|
| Alkane | Helium SD | Nitrogen SD |
| Eicosane | 0.066 | 0.052 |
| Nonadecane | 0.071 | 0.059 |
| Octadecane | 0.099 | 0.143 |
| Heptadecane | 0.100 | 0.075 |
| Hexadecane | 0.198 | 0.095 |
| Pentadecane | 0.204 | 0.005 |
| Tetradecane | 0.130 | 0.108 |
| Tridecane | 0.359 | 0.127 |
| Dodecane | 0.009 | 0.129 |
| Undecane | 0.170 | 0.009 |
| Decane | 0.009 | 0.127 |
| Nonane | 0.000 | 0.226 |
| Octane | 0.014 | 0.113 |
| Heptane | 0.014 | 0.057 |
| SD=unitless | | |

Table 7: Standard Deviations for the retention times of the triplicate alkane testing at 15°C/min.

| **Table 8: $t_R$ Standard Deviations for Rate 20°C/min** | | |
|---|---|---|
| Alkane | Helium SD | Nitrogen SD |
| Eicosane | 0.057 | 0.102 |
| Nonadecane | 0.142 | 0.064 |
| Octadecane | 0.189 | 0.000 |
| Heptadecane | 0.184 | 0.000 |
| Hexadecane | 0.106 | 0.097 |
| Pentadecane | 0.109 | 0.099 |
| Tetradecane | 0.128 | 0.109 |
| Tridecane | 0.009 | 0.123 |
| Dodecane | 0.021 | 0.118 |
| Undecane | 0.000 | 0.000 |
| Decane | 0.014 | 0.141 |
| Nonane | 0.000 | 0.184 |
| Octane | 0.094 | 0.088 |
| Heptane | 0.078 | 0.037 |
| SD=unitless | | |

Table 8: Standard Deviations for the retention times of the triplicate alkane testing at 20°C/min.

### *3.2 Van Deemter Plots*

The next experiment that was completed was an isothermal tetradecane, $C_{14}$, analysis under both helium and nitrogen carrier gases. The isothermal trials were ran at pressures of 30, 40, 50,60, 70, 80, and 90 psi and Van Deemter curves were created. The isothermal temperatures tested was 180°C and the split ratio was 20:1.

#### *3.2.1 Helium and Nitrogen $C_{14}$ Fundamental Calculations*

Fundamental calculations to measure column performance such as retention time ($t_R$), efficiency (N), plate height (H), and linear velocity (μ) were performed. The column length was 3000cm. As the temperature increased, the retention time and plate height decreased while the efficiency and linear velocity increased. This trend was amplified more when the pressure was increased. The following contains the data for the helium and nitrogen $C_{14}$ separations at three different pressures.

Tables 9 and 10 show some basic calculations performed for the isothermal run of tetradecane under both helium and nitrogen gases. The retention times were shorter when using nitrogen while the efficiencies were slightly higher for helium. This is the opposite of what the literature suggests, having nitrogen as the more efficient carrier gas and helium as the faster one. Furthermore, the plate heights were very similar and the linear velocities were higher for nitrogen. This was especially the case as the pressure was increased. As the pressure increased, the retention times decreased while the linear velocity increased which was expected.

| Table 9: $C_{14}$ Helium Fundamental Calculations at 180°C | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Parameter** | **30 psi** | **40 psi** | **50 psi** | **60 psi** | **70 psi** | **80 psi** | **90 psi** |
| $t_R$ (min) | 2.09 | 1.61 | 1.33 | 1.22 | 0.988 | 0.870 | 0.782 |
| $t_m$ (min) | 1.18 | 0.913 | 0.776 | 0.720 | 0.563 | 0.497 | 0.448 |
| N (unitless) | 104081 | 86009 | 45693 | 38166 | 35416 | 33547 | 27104 |
| H (cm) | 0.029 | 0.035 | 0.066 | 0.079 | 0.085 | 0.089 | 0.111 |
| μ (cm/sec) | 42.2 | 54.7 | 64.4 | 69.4 | 88.8 | 100.6 | 111.6 |
| $t_m$ peak width (min) | 0.033 | 0.026 | 0.040 | 0.040 | 0.024 | 0.021 | 0.019 |
| $t_R$ peak width (min) | 0.026 | 0.022 | 0.025 | 0.026 | 0.021 | 0.019 | 0.019 |

Table 9: Tetradecane under helium carrier gas at varying pressures.

| Table 10: $C_{14}$ Nitrogen Fundamental Calculations at 180°C | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Parameter** | **30 psi** | **40 psi** | **50 psi** | **60 psi** | **70 psi** | **80 psi** | **90 psi** |
| $t_R$ (min) | 1.93 | 1.49 | 1.22 | 1.038 | 0.898 | 0.806 | 0.719 |
| $t_m$ (min) | 1.11 | 0.859 | 0.707 | 0.604 | 0.525 | 0.474 | 0.424 |
| N (unitless) | 82518 | 56987 | 38103 | 29929 | 22400 | 18045 | 14360 |
| H (cm) | 0.036 | 0.053 | 0.079 | 0.100 | 0.134 | 0.166 | 0.209 |
| μ (cm/sec) | 45.0 | 58.2 | 70.7 | 82.7 | 95.2 | 105.4 | 117.9 |
| $t_m$ peak width (min) | 0.037 | 0.033 | 0.030 | 0.028 | 0.026 | 0.027 | 0.025 |
| $t_R$ peak width (min) | 0.027 | 0.025 | 0.025 | 0.024 | 0.024 | 0.024 | 0.024 |

Table 10: Tetradecane under nitrogen carrier gas at varying pressures.

In conclusion, the lower pressures have longer retention times because the lack of force causes tetradecane to elute much slower in the column. The linear velocities increased with increased pressure which was expected because the carrier gas flow was amplified. The plate height is linearly related to the velocity which was also seen in the data. The higher velocities had the highest plate heights. By comparing the number values for helium and nitrogen, it is clear that the separations are very similar. Nitrogen had shorter retention times for majority of the analysis and had shorter analysis times for both the isothermal and the temperature programming experiments.

### *3.2.2 Van Deemter Curve*

As previously mentioned, Van Deemter curves are used to characterize column performance and to determine an optimum velocity for the most effective gas chromatographic separations. According to literature, helium has an optimum between 20-40cm/sec while nitrogen has an optimum between 10-20cm/sec. The isothermal $C_{14}$ fundamental calculations were used to create Van Deemter curves for both carrier gases. The goal was to confirm that previously published Van Deemter curves, such as Figure 3, are valid for capillary columns. Van Deemter curves were originally constructed for packed columns and many adjustments have been made over the years.

Figure 12 shows the Van Deemter curves for tetradecane under helium and nitrogen carrier gases at pressures of 30, 40, 50, 60, 70, 80, and 90 psi. As shown by the curve below, the lowest point on the graph for helium and nitrogen, or the optimum velocity, is at a linear velocity of 40cm/sec and 45cm/sec respectivetly for the pressures tested. This is the expected linear velocity for helium based on previous literature (20-40cm/sec) but a higher than expected linear velocity for nitrogen (10-20cm/sec). The Van Deemter curve was later extrapolated in figure 13 and a further analysis was conducted.

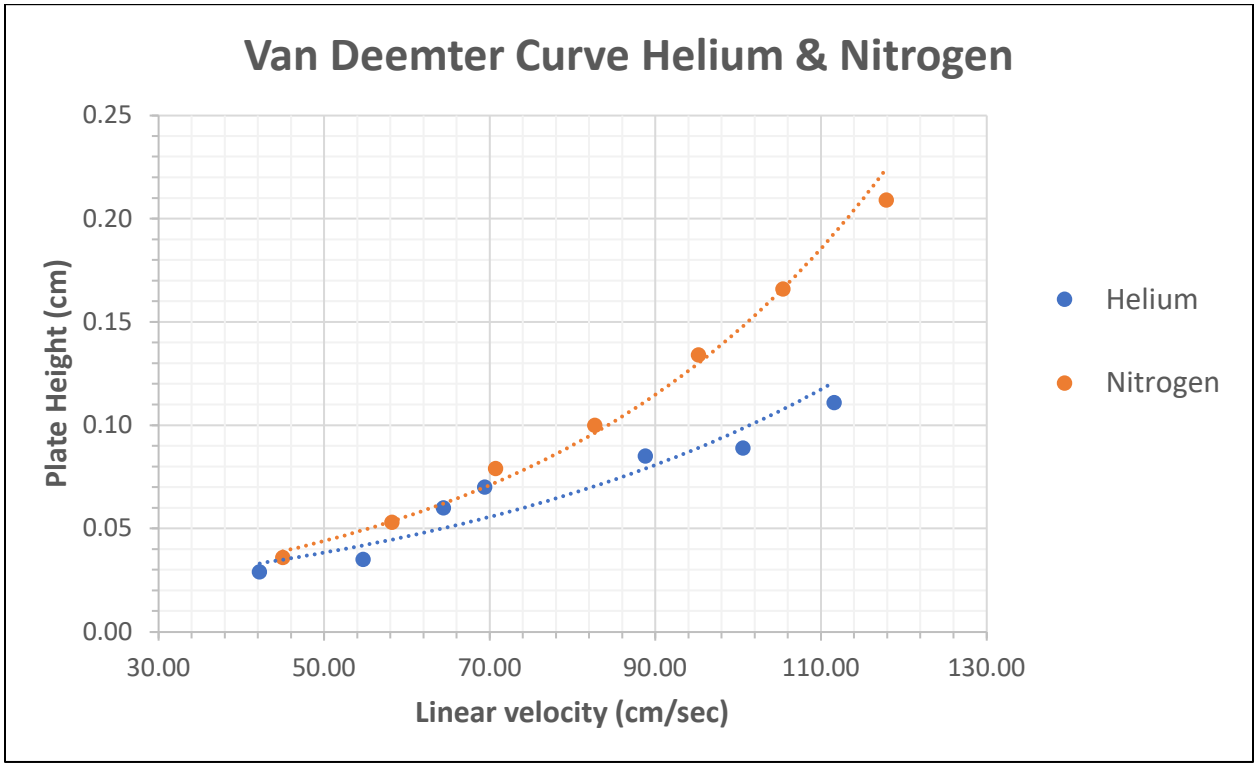



Figure 12: Van Deemter curve for helium and nitrogen at 180°C with a split ratio of 20:1.

Figure 13 shows the extrapolated Van Deemter curve for tetradecane under helium and nitrogen carrier gas at pressures below 30 psi. Orginally, it was thought that any pressure tested below 30 psi was too flat of a line which proved that the the mass transfer region of the Van Deemter equation was not reached yet and the experimental pressure needed to be increased. However, by extrapolating the curve backwards, it is clear that the linear velocities decrease. This favors nitrogen as the expected linear velocity region for this carrier gas is 10-20cm/sec.

The helium Van Deemter curve showed some variability which brings into question the validity of the Van Deemter equation. The variability could be due to general noise from the experiment but further research should include a statistical analysis such as non-linear least squares or residual plots to better fit the data to the Van Deemter equation. However, nitrogen did not show these same trends. Nitrogen did not see this variability which proves that the assumptions about the Van Deemter equation are true. It was also concluded that nitrogen is a better carrier gas for capillary gas chromatography since it was better fit to the actual equation. In the end, this isothermal experiment demonstrated that the performance and optimium linear velocities obtained for both helium and nitrogen in this research were not ideal, but similar enough to the optimium velocities published in previous Van Deemter carrier gas studies.

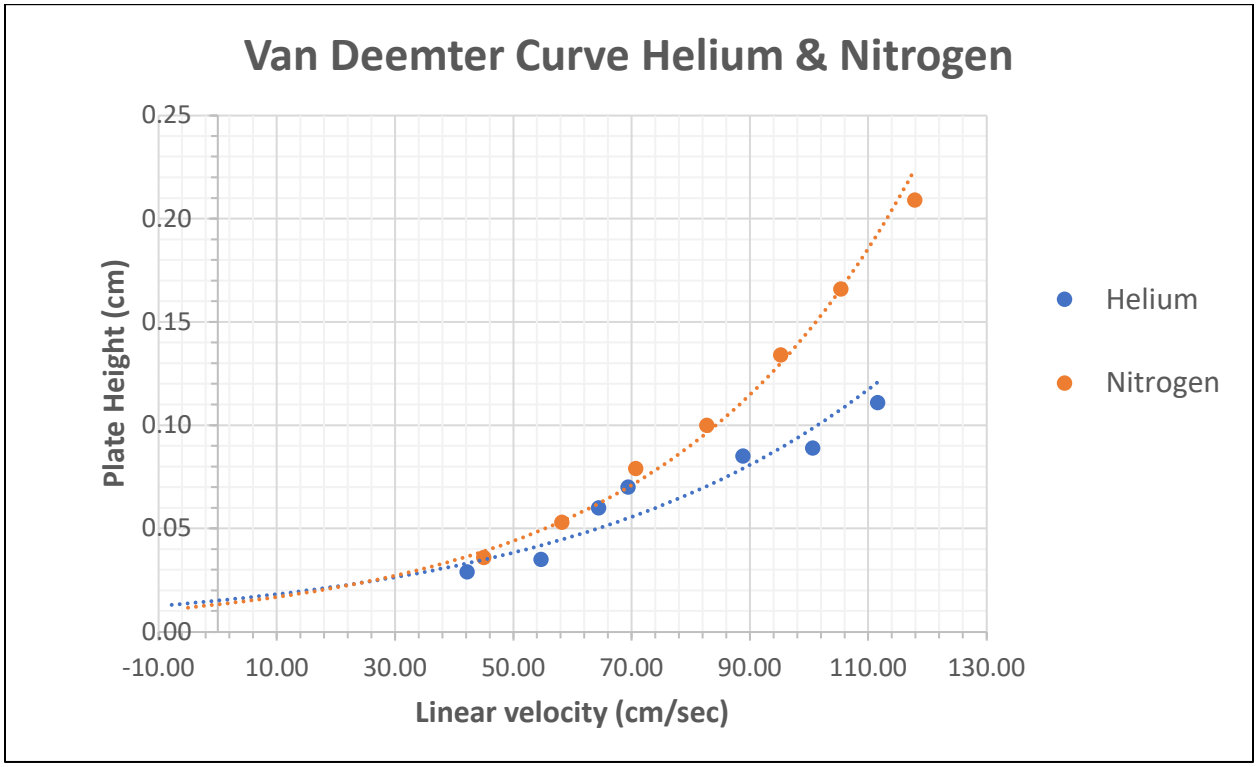



Figure 13: Van Deemter curve extraploated for helium and nitrogen.

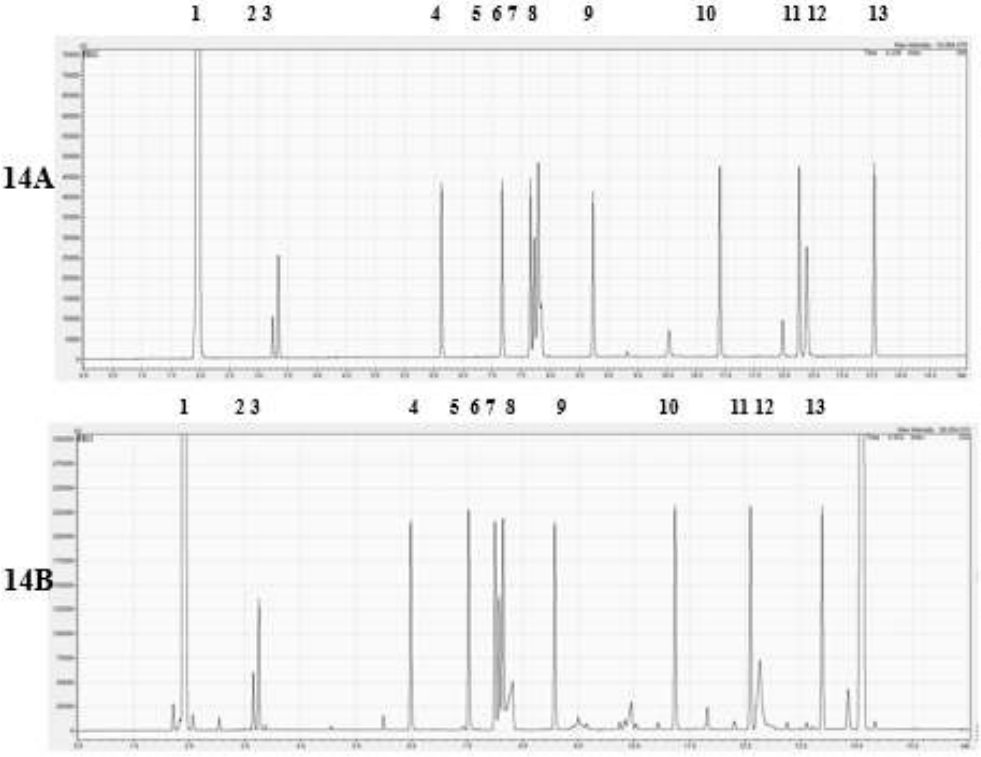
### *3.3 Grob Test Mixture Analysis*

The following data contains the results for the separation and analysis of the Grob test mixture under both helium and nitrogen carrier gases. Each experiment was conducted twice, once with a split ratio of 50:1 and again with a split ratio of 15:1. The 14-minute peaks seen in the nitrogen analysis were leftover solvent run in between trials to ensure the column was clean. Separation numbers were the parameters chosen to compare column performance because Grob himself used these values in his originial 1981 paper.[12] He labeled these as TZ, or trennzahl, which is the German symbol to express separation numbers. Below is the separation data for the Grob test mixture.

#### *3.3.1 Helium and Nitrogen Chromatographic Separations*

Figures 14 and 15 show the Grob test mixture separations with a split of 50:1 and 15:1 for both carrier gases. All 13 components of the test mixture were eluted in under 15 minutes. Nitrogen had slightly shorter analysis times when compared to helium. In addition, helium had a clean baseline with limited noise and only a few small impurities. However, unlike helium, the nitrogen carrier gas was able to pick up a lot more impurities near the baseline. It was able to uncover smaller peaks that were not shown at all with the helium analysis. This shows that nitrogen has a higher sensitivity when compared against helium. Even though this makes the chromatogram look less favorable compared to helium, it shows the effectiveness of the gas. Overall, there were no major issues of peak fronting or tailing and the separations of the compounds were successful. The following data shows the chromatograms for the Grob test mixture.

# Figure 14: Grob Test Mixture @ 50:1 Split Ratio



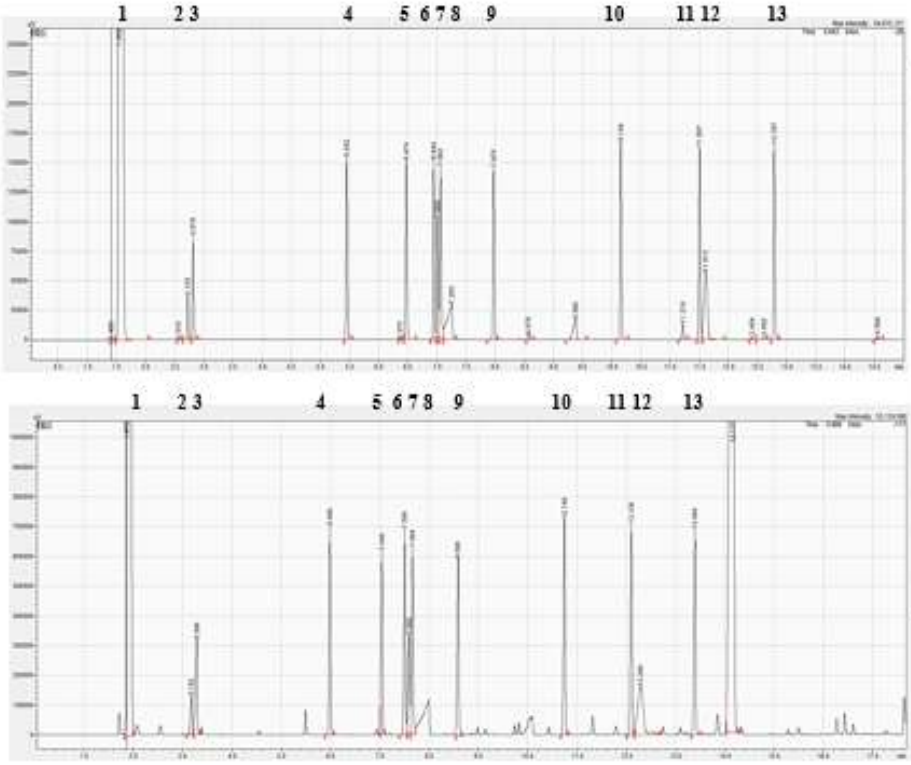

| Peak # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| 13-12 | 15.8 | 9.08 | 1-Dichloromethane solvent |
| 12-11 | 0.880 | 0.530 | 2- 2,3-Butanediol |
| 11-10 | 24.2 | 20.2 | 3- n-Decane |
| 10-9 | 38.5 | 33.9 | 4- n-Undecane |
| 9-8 | 14.9 | 14.3 | 5- 1-Octanol |
| 8-7 | 0.170 | 0.130 | 6- 2-Ethylhexanoic acid |
| 7-6 | 0.230 | 0.190 | 7- 1-Nonanal |
| 6-5 | 8.31 | 6.58 | 8- 2,6-Dimethylphenol |
| 5-4 | 19.4 | 16.7 | 9- 2,6-Dimethylaniline |
| 4-3 | 57.3 | 47.8 | 10- Methyl decanoate |
| 3-2 | 1.02 | 0.870 | 11- Internal standard |
| 2-1 | 20.1 | 17.6 | 12- Dicyclohexylamine |
| SN: unitless | | | 13- Methyl laurate |

Figure 14: The Grob test mixture separated under helium (14A) and nitrogen (14B) and respective separation numbers for the analysis. SN is unitless.

The data above shows the separation of the Grob test mixture using both helium and nitrogen carrier gases. Figure 14A is the helium analysis where Figure 14B is the nitrogen analysis. Nitrogen eluted the test mixture with shorter total analysis times when compared to helium. Nitrogen was also able to detect more impurities near the baseline that were not detected with helium. This is very beneficial and important when trying to find impurities in samples. It shows the sensitivity and the efficiently of nitrogen as a GC carrier gas. For the 50:1 split ratio experiment, helium had slightly higher separation numbers when compared to nitrogen. However, the differences between the values are very close and comparable. The compounds that had high separation numbers with helium also had high values with nitrogen. The compounds that had low values with helium also had low values with nitrogen. In the end, the performance of nitrogen was very similar to helium.

The data below shows the separation of the Grob test mixture under both helium and nitrogen carrier gases with a different split ratio. Figure 15A is the helium analysis where Figure 15B is the nitrogen analysis. Helium eluted the analytes at shorter total analysis times, but the difference in analysis times between the gases were less than 1.5 minutes. This is minimal when considering the efficiency of the separation. Once again, nitrogen was able to reveal components near the baseline that were not eluted with the helium gas. Like the 50:1 split ratio, helium had higher separation numbers, but nitrogen was very close. The values were comparable and even had the same exact value for the peaks 8-7. To sum up, both helium and nitrogen carrier gases were able to successfully separate the 13-component the Grob test mixture with similar chromatographic properties, similar separation numbers, and overall similar column performance.

# Figure 15: Grob Test Mixture @ 15:1 Split Ratio




| Peak # | Helium SN | Nitrogen SN | Peak Key |
|---|---|---|---|
| 13-12 | 11.4 | 5.99 | 1-Dichloromethane solvent |
| 12-11 | 0.110 | 0.17 | 2- 2,3-Butanediol |
| 11-10 | 24.5 | 18.4 | 3- n-Decane |
| 10-9 | 40.1 | 30.2 | 4- n-Undecane |
| 9-8 | 15.6 | 12.6 | 5- 1-Octanol |
| 8-7 | 1.00 | 1.00 | 6- 2-Ethylhexanoic acid |
| 7-6 | 0.270 | 0.190 | 7- 1-Nonanal |
| 6-5 | 8.04 | 5.57 | 8- 2,6-Dimethylphenol |
| 5-4 | 19.4 | 14.8 | 9- 2,6-Dimethylaniline |
| 4-3 | 53.9 | 37.6 | 10- Methyl decanoate |
| 3-2 | 0.980 | 0.290 | 11- Internal standard |
| 2-1 | 16.3 | 11.2 | 12- Dicyclohexylamine |
| SN: unitless | | | 13- Methyl laurate |

Figure 15: The Grob test mixture separated under helium (15A) and nitrogen (15B) and respective separation numbers for the analysis. SN is unitless.

In the end, the purpose of the Grob test mixture was to optimize chromatographic conditions, obtain information about column quality, and quantitate/compare results. Experimental parameters such as isothermal testing, column length, column film thickness, chemical volatilities, and conditions such as split ratio, temperature, and flow in addition to analysis models such as separation numbers, or Trennzahl, were all followed directly from Grob's original paper. The only condition that was modified was the carrier gases. With that said, the elution order and elution time were the same as Grob's original paper despite whether helium or nitrogen was used. Both carrier gases performed the same, making nitrogen a viable option for an alternative carrier gas.

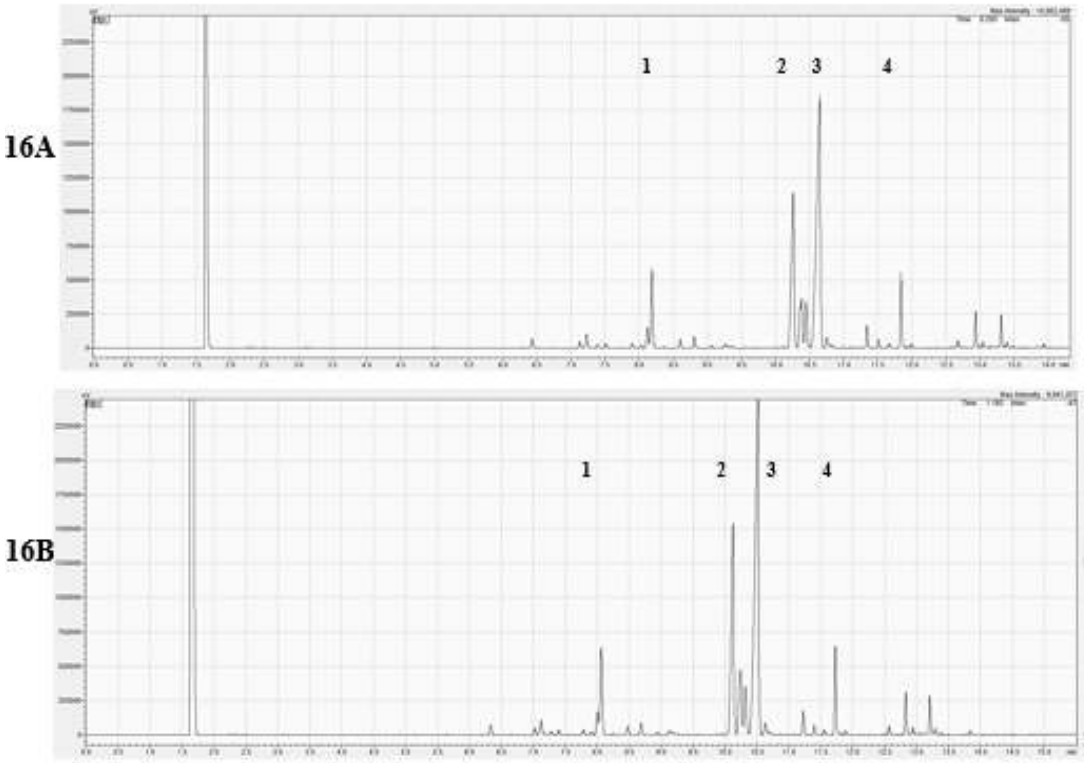
### *3.4 Essential Oils Analysis*

The next analysis performed was the separation of complex mixtures such as essential oils. Besides for alkanes and the Grob test mixture components, this was another group of chemicals that were tested with different carrier gases. Each oil was run on the instrument under helium and nitrogen to see which carrier gas can more efficiently separate the components. Characterization of the oils was not performed as the focus was on fundamental separations. Below is the data for both gases.

#### *3.4.1 Helium and Nitrogen Chromatographic Separations*

The four complex mixtures of peppermint, lavender, eucalyptus and patchouli oils were all tested. The peppermint, patchouli, and lavender oils were all complex and contained multiple components besides for the main ingredient. The eucalyptus oil was the purest of all the oils and only showed one main peak. These oils were separated with helium and compared with nitrogen. The chromatograms were almost identical, with all peaks eluting the same way on both gases and nitrogen having shorter retention times. These separations are shown below.

# Figure 16: Peppermint Oil




| Peak # | Helium SN | Nitrogen SN |
|---|---|---|
| 4-3 | 28.6 | 25.4 |
| 3-2 | 2.61 | 2.60 |
| 2-1 | 12.7 | 12.9 |
| SN: unitless | | |

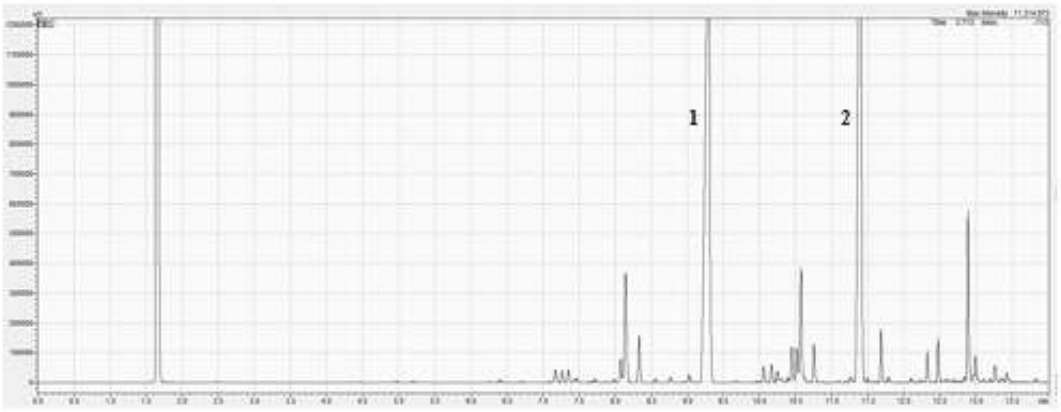
Figure 16: Peppermint oil separated under helium (16A) and nitrogen (16B) and respective separation numbers for the analysis. SN is unitless.

Figure 16 shows the separation of peppermint oil using either helium or nitrogen carrier gases. Figure 16A is the helium separation while Figure 16B is the nitrogen separation. Like the previous experiments, nitrogen and helium carrier gases had similar chromatographic properties. Retention times were close, peak shapes were the same, and elution order was identical. Nitrogen did elute the oil faster, with shorter retention times for every peak. Additionally, the separation numbers were very comparable. A later analysis (see Figure 20) expanded the critical region on both chromatograms and resolution values were analyzed. Overall, like the alkane analysis and the Grob test mixture analysis, both carrier gases performed the same which proves that nitrogen can be considered a reasonable GC carrier gas.

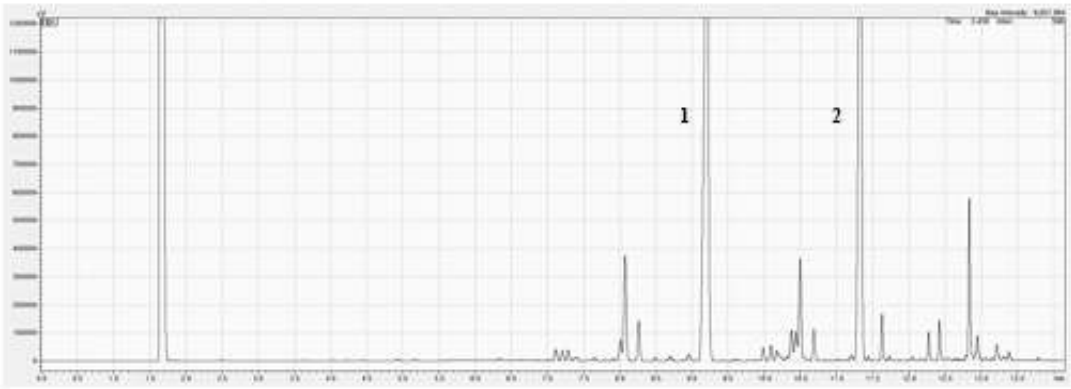
Figure 17 shows the separation of lavender oil under both helium and nitrogen carrier gases. Figure 17A is the helium separation while Figure 17B is the nitrogen separation. Like the previous experiments throughout this research, both carrier gases had similar chromatographic properties. Retention times were close, peak shapes were the same, and elution order was identical. The lavender oil separation in Figure 17B shows nitrogen out-performing helium with shorter retention times for every peak. The separation number were, once again, close in value and very comparable. In the end, there is no doubt that nitrogen can separate these oils almost identical, and slightly faster, when compared to helium chromatographically and numerically.

# Figure 17: Lavender Oil

17A




17B

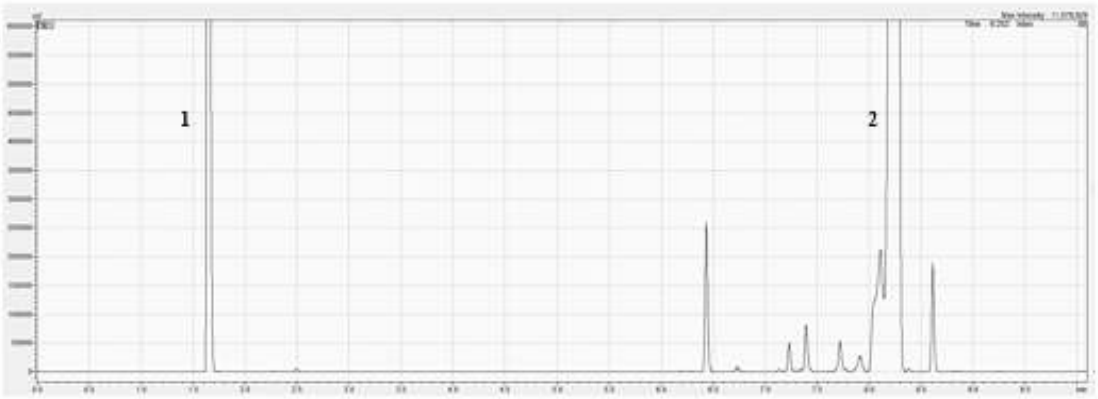



| Peak # | Helium SN | Nitrogen SN |
|---|---|---|
| 2-1 | 19.2 | 19.8 |
| SN: unitless | | |

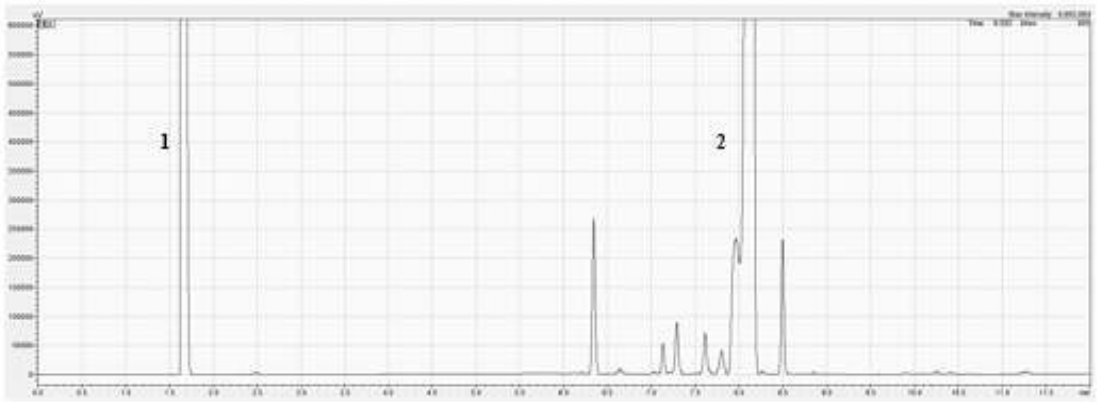
Figure 17: Lavender oil separated under helium (17A) and nitrogen (17B) and respective separation numbers for the analysis. SN is unitless.

# Figure 18: Eucalyptus Oil

18A




18B



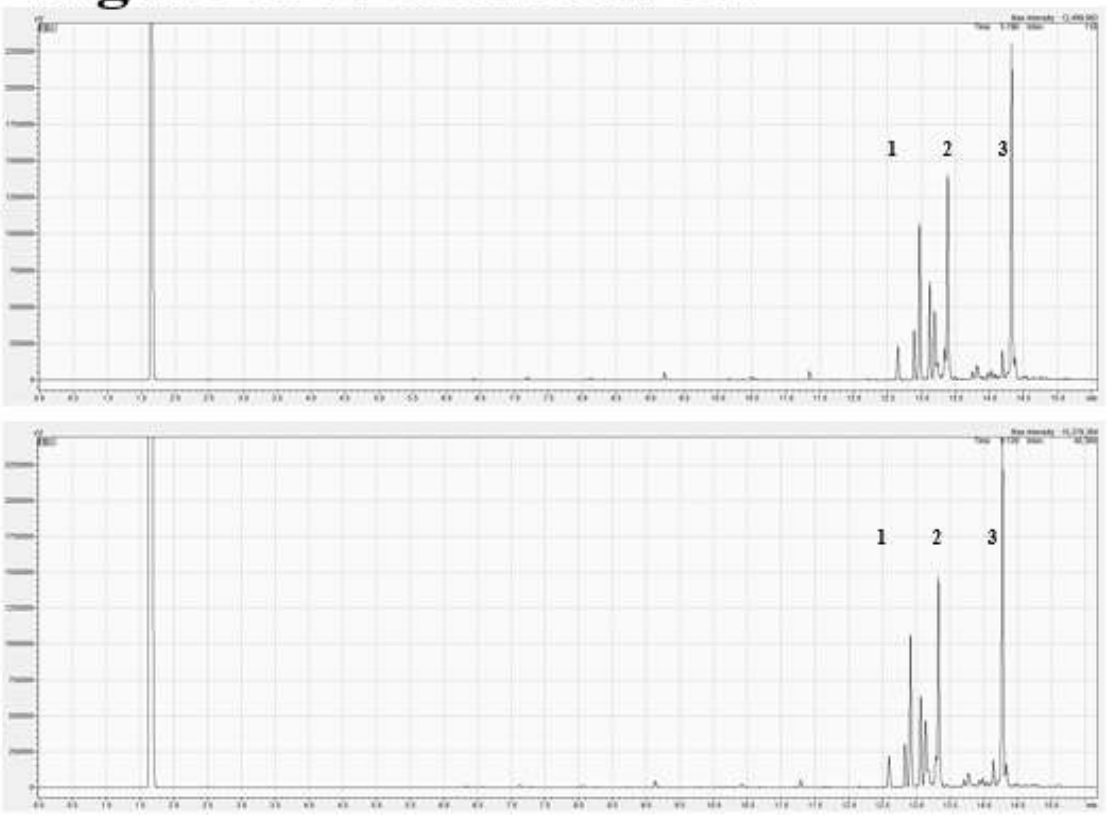

| Peak # | Helium SN | Nitrogen SN |
|---|---|---|
| 2-1 | 64.7 | 65.4 |
| SN: unitless | | |

Figure 18: Eucalyptus oil separated under helium (18A) and nitrogen (18B) and respective separation numbers for the analysis. SN is unitless.

Figure 18 shows the separation of eucalyptus oil under both helium and nitrogen carrier gases. Figure 18A is the helium separation while Figure 18B is the nitrogen separation. Like the previous oil separations, both helium and nitrogen had similar chromatographic properties. Retention times were close, peak shapes were the same, and elution order was identical. The eucalyptus oil also followed similar trends as the other oils with nitrogen eluting the main ingredient slightly faster. The solvent peak, dichloromethane, was used for the separation number analysis and compared against the one eluted peak. These values were, once again, very close in value. In the end, the data collected proves that nitrogen can be an alternative carrier gas for the very limited helium gas.

Figure 19 shows the separation of patchouli oil under both helium and nitrogen carrier gases. Figure 19A is the helium separation while Figure 19B is the nitrogen separation. Both helium and nitrogen had similar chromatographic properties. Retention times were close, peak shapes were the same, and elution order was identical. A later analysis, see Figure 21, expanded the critical region on both chromatograms and resolution values were analyzed. The separation numbers above also show the similar performance of the carrier gases. In conclusion, like the alkane analysis, the Grob test mixture analysis, and the three essential oil testing, both carrier gases performed the same which proves that nitrogen can be considered an excellent GC carrier gas.

# Figure 19: Patchouli Oil




| Peak # | Helium SN | Nitrogen SN |
|---|---|---|
| 3-2 | 8.15 | 8.39 |
| 2-1 | 18.2 | 18.4 |
| SN: unitless | | |

Figure 19: Patchouli oil separated under helium (19A) and nitrogen (19B) and respective separation numbers for the analysis. SN is unitless.

### *3.4.2 Critical Point Resolution*

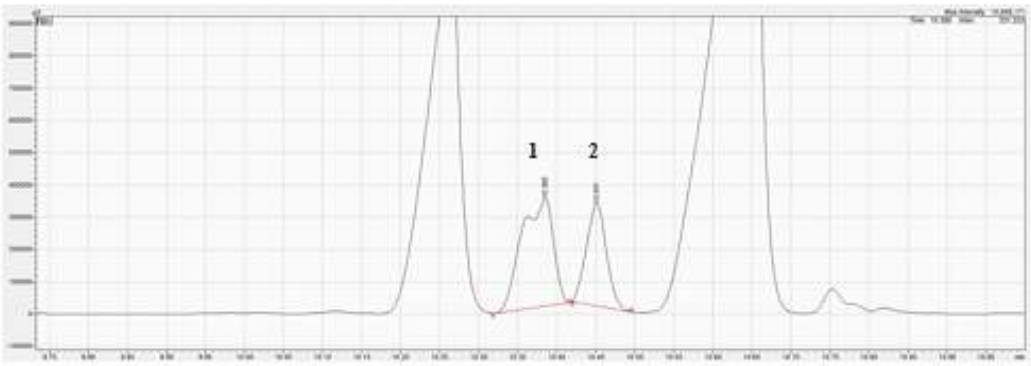
Peppermint oil and patchouli oil were two complex mixtures that had critical regions which could further be analyzed to determine carrier gas performance. The critical region is made up of a critical pair which represents two components with the lowest calculated resolution between them. This is useful information when determining the effectiveness of a chromatographic separation. Below are the chromatograms and resolution calculations for helium and nitrogen critical pairs.

Figure 20 shows the critical region of peppermint oil separations by both helium and nitrogen carrier gases. Figure 20A shows the helium separation of the critical pair with a resolution of 1.671. Figure 20B shows the nitrogen separation of the critical pair with a resolution of 1.711. Both components are baseline resolved since the values are above 1.500. Nitrogen had a higher critical pair resolution meaning that the separation of peppermint oil was slightly better with the nitrogen carrier gas when compared with the helium carrier gas.

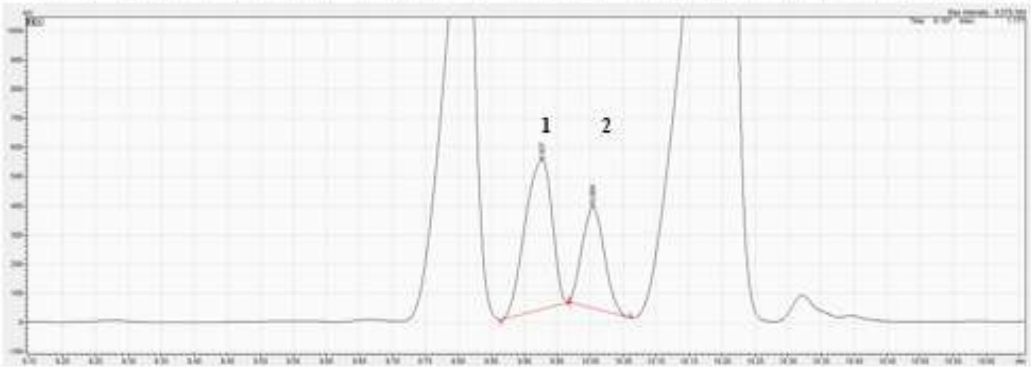
Figure 21 shows the critical region of peppermint oil separations by both helium and nitrogen carrier gases. Figure 21A shows the helium separation of the critical pair with a resolution of 2.824. Figure 21B shows the nitrogen separation of the critical pair with a resolution of 2.561. Both components are baseline resolved since the values are above 1.500. Helium had a higher critical pair resolution meaning that the separation of patchouli oil was slightly better with the helium carrier gas. However, the difference was minimal, being only 0.263 apart.

# Figure 20: Peppermint Oil Critical Pair

20A




20B



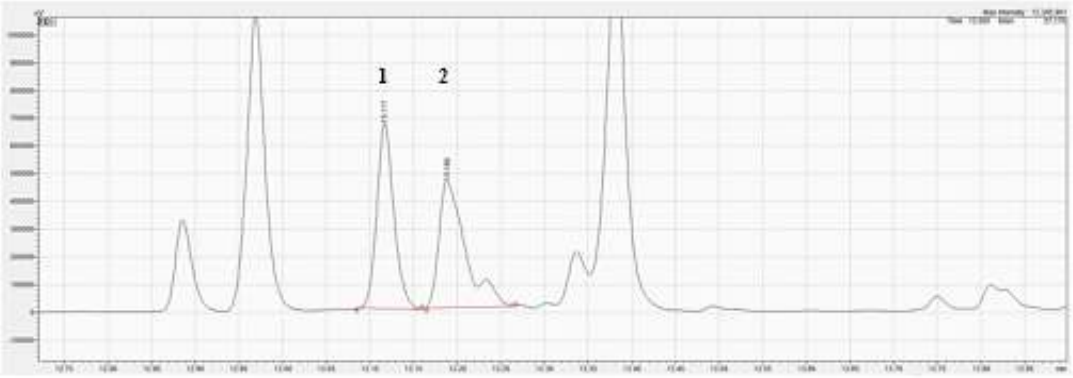

| Peak # | Helium ($R_s$) | Nitrogen ($R_s$) |
|---|---|---|
| Critical Pair 2-1 | 1.67 | 1.71 |

Figure 20: Critical pairs for helium (20A) and nitrogen (20B) and respective resolution values.

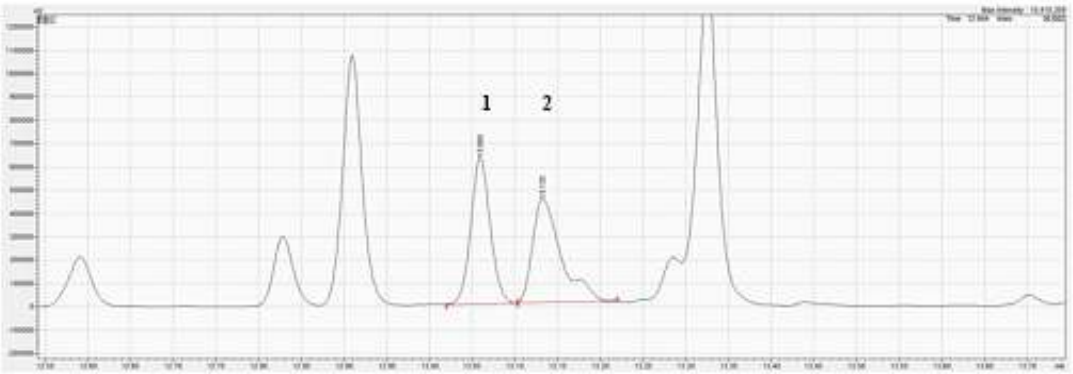
Resolution is unitless.

# Figure 21: Patchouli Oil Critical Pair

21A




21B




| Peak # | Helium ($R_s$) | Nitrogen ($R_s$) |
|---|---|---|
| Critical Pair 2-1 | 2.82 | 2.56 |

Figure 21: Critical pairs for helium (21A) and nitrogen (21B) and respective resolution values.

Resolution is unitless

In the end, critical pair resolution helps to determine how effective a separation was. For both critical regions, helium and nitrogen had similar resolution values with nitrogen eluting the oils with shorter retention times. This was another gas chromatographic application where nitrogen gas demonstrated how effective and successful it could be in capillary column separations.

### *3.5 PAH Analysis*

The final class of compounds evaluated in this research were PAHs. A mixture of 16 PAHs were separated under both helium and nitrogen carrier gases. The separations were compared both chromatographically and mathematically just like the previous alkane, Grob test mixture, and essential oil experiments. Similar trends were once again observed where nitrogen and helium had comparable performance tendencies. Critical regions were expanded, and the resolutions of the critical pairs were calculated. All 16 chemicals of the mixture were successfully eluted under both carrier gases. Below is the Restek published chromatogram of the expected separation. The elution order, is as followed: naphthalene, acenaphthylene, acenaphthene fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-CD)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene in a methylene chloride/methanol solvent.

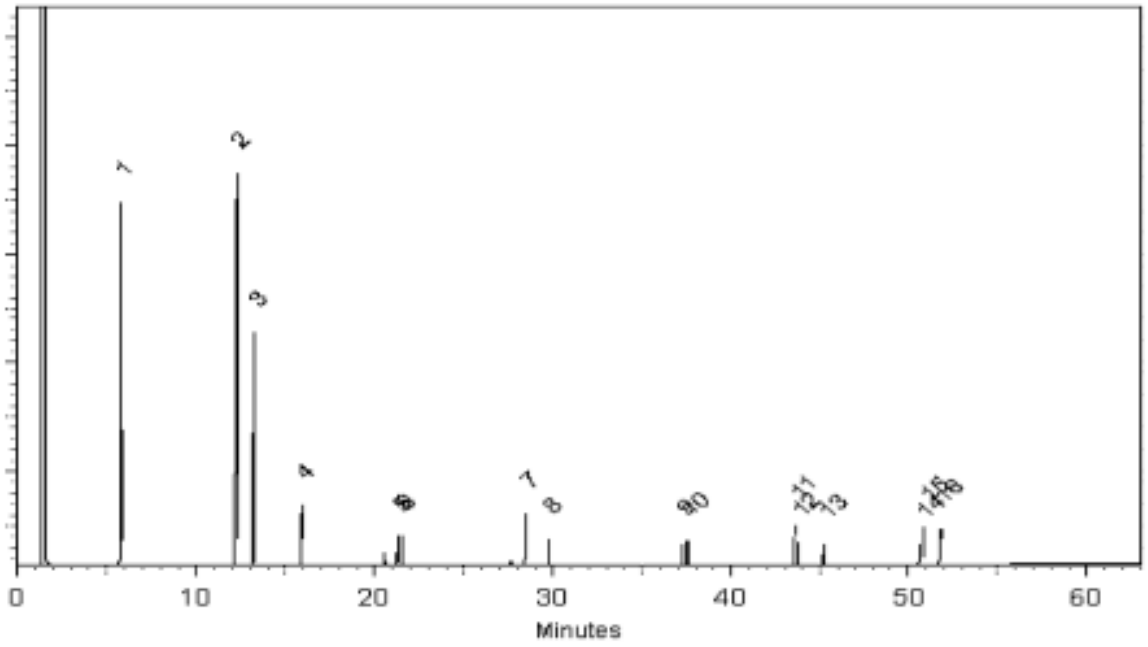
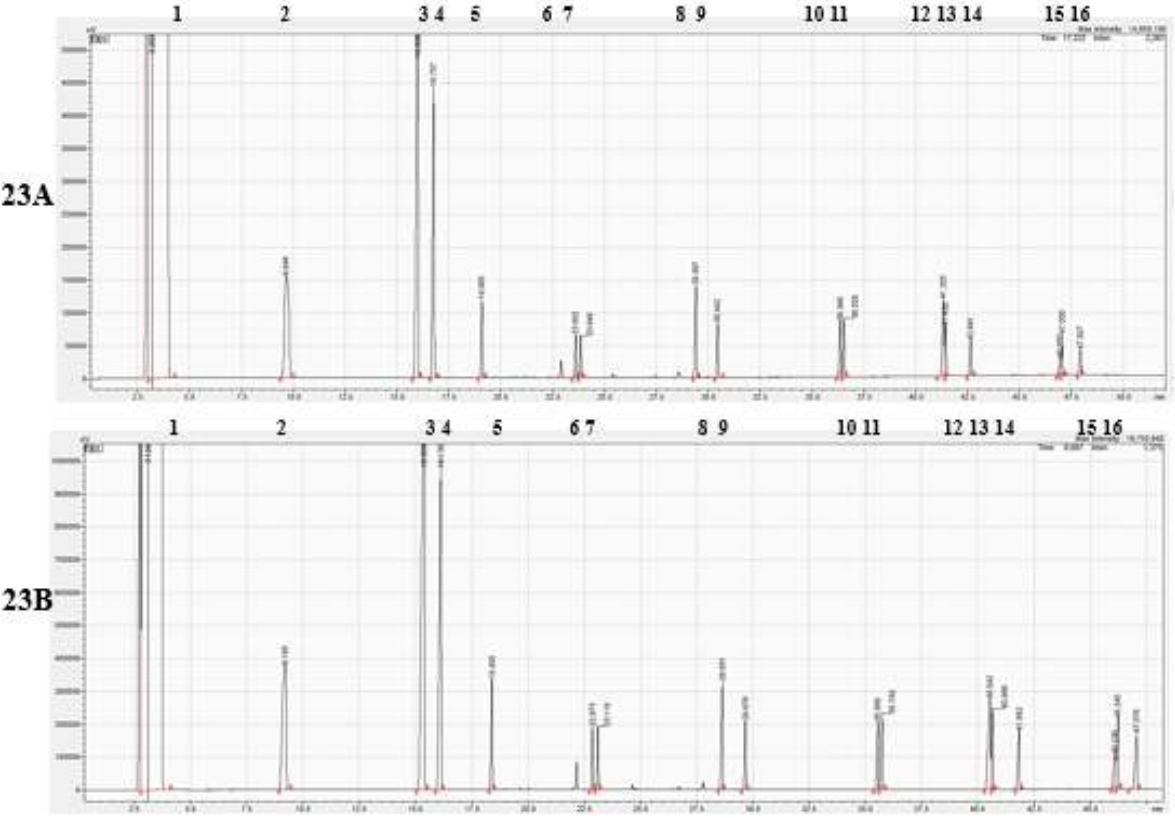



Figure 22: Restek chromatogram of expected PAH mixture separation.[34]

### *3.5.1 Helium and Nitrogen Chromatographic Separations*

Figure 23 shows the PAH test mixture separated under helium and nitrogen carrier gases. Figure 23A shows the separation with helium while Figure 23B shows the separation with nitrogen. All 16 components of the test mixture were cleanly separated in under 48 minutes. Nitrogen eluted the PAH mixture slightly faster with shorter total analysis times when compared to helium. The peaks had no peak deformation such as fronting or tailing and the baseline had limited noise. The critical regions of the PAH analysis were expanded, see Figure 24, and resolutions were calculated. Overall, the chromatograms were extremely similar and very comparable for both carrier gases.

# Figure 23: PAH Separation




| Peak Number | Peak Key |
|---|---|
| 1 | Naphthalene |
| 2 | Acenaphthylene |
| 3 | Acenaphthene |
| 4 | Fluorene |
| 5 | Phenanthrene |
| 6 | Anthracene |
| 7 | Fluoranthene |
| 8 | Pyrene |
| 9 | Benzo(a)anthracene |
| 10 | Chrysene |
| 11 | Benzo(b)fluoranthene |
| 12 | Benzo(k)fluoranthene |
| 13 | Benzo(a)pyrene |
| 14 | Indeno(1,2,3-CD)pyrene |
| 15 | Dibenz(a,h)anthracene |
| 16 | Benzo(g,h,i)perylene |

Figure 23: PAH separation under helium (23A) and nitrogen (23B).

### *3.5.2 Critical Point Resolution*

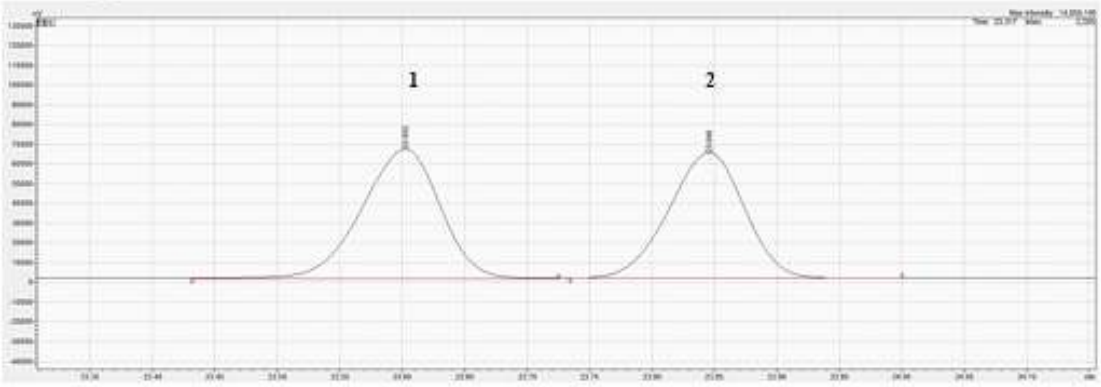
The PAH solution was another complex mixture that had critical regions which could further be analyzed to determine carrier gas performance. The critical region is made up of a critical pair which represents two components with the lowest calculated resolution between them. This is useful information when determining the effectiveness of a chromatographic separation. Below are the chromatograms and resolution calculations for helium and nitrogen critical pairs.

Figure 24 shows the critical region of peppermint oil separations by both helium and nitrogen carrier gases. Figure 24A shows the helium separation of the critical pair with a resolution of 3.669. Figure 24B shows the nitrogen separation of the critical pair with a resolution of 4.495. Both components are baseline resolved since the values are above 1.500. Nitrogen had a much higher critical pair resolution meaning that the separation using nitrogen was much more effective.

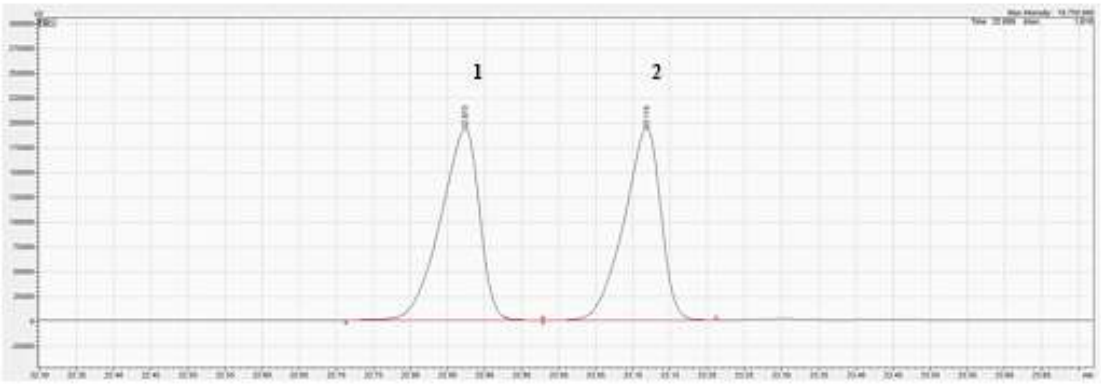
Figure 25 shows the critical region of peppermint oil separations by both helium and nitrogen carrier gases. Figure 25A shows the helium separation of the critical pair with a resolution of 2.373. Figure 25B shows the nitrogen separation of the critical pair with a resolution of 2.652. Both components are baseline resolved since the values are above 1.500. Once again, nitrogen had a higher critical pair resolution establishing that the separation using nitrogen was much more effective. In the end, critical pair resolution helps to determine how effective a separation was. For both critical regions, helium and nitrogen had similar resolution values, but nitrogen actually had higher values all around. This proves that even a baseline separation is more affective using nitrogen as a GC carrier gas. Nitrogen also had shorter retention times. This was the final gas chromatographic application where nitrogen gas demonstrated how effective and successful it could be in capillary column separations.

# Figure 24: PAH Critical Pair #1

24A




24B



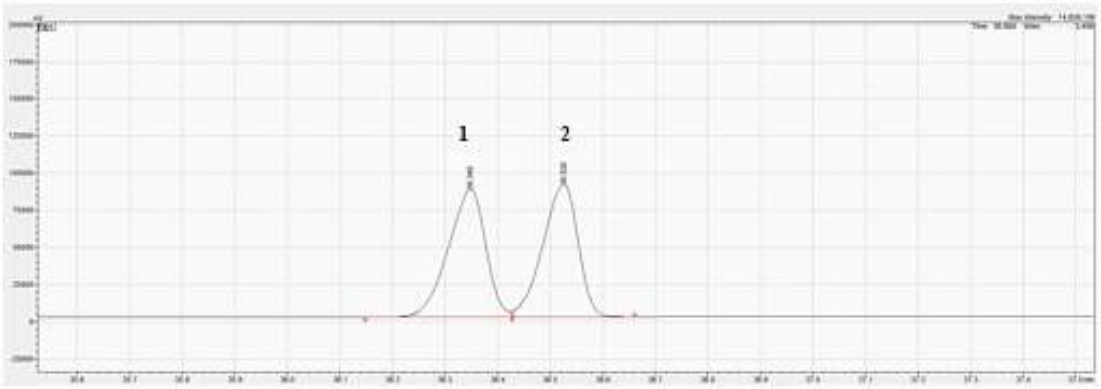

| Peak # | Helium ($R_s$) | Nitrogen ($R_s$) |
|---|---|---|
| Critical Pair 2-1 | 3.67 | 4.50 |

Figure 24: Critical pairs for helium (24A) and nitrogen (24B) and respective resolution values.

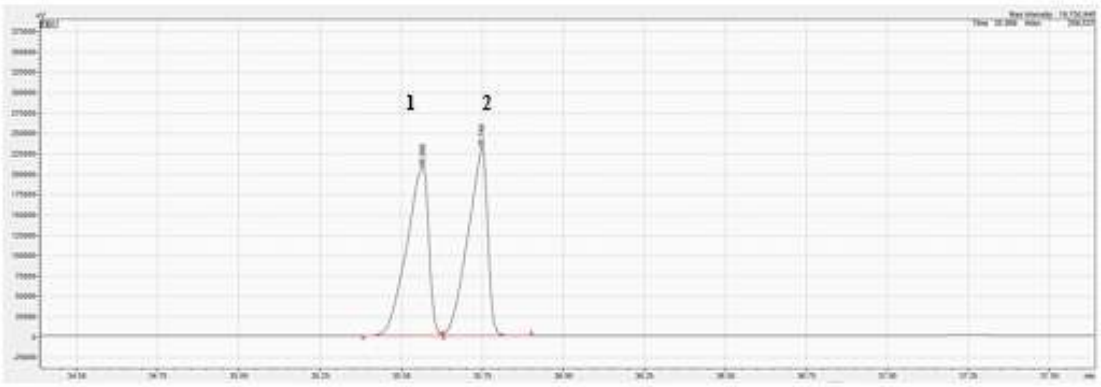
Resolution is unitless

# Figure 25: PAH Critical Pair #2

25A




25B




| Peak # | Helium ($R_s$) | Nitrogen ($R_s$) |
|---|---|---|
| Critical Pair 2-1 | 2.37 | 2.65 |

Figure 25: Critical pairs for helium (25A) and nitrogen (25B) and respective resolution values.

Resolution is unitless

### *4. Research Conclusions*

In conclusion, the objectives of this research were accomplished. The data was able to prove that nitrogen should be deemed a superior alternative carrier gas to replace helium. With helium becoming more limited and expensive as the days go by, it was important to explore alternatives and determine if nitrogen could perform like helium. Throughout the experiments, it was clear that nitrogen does function like helium and is able to separate different groups of chemicals better then how helium separates them. This is promising for the future of GC carrier gases.

To begin, the alkane separations showed how similar helium and nitrogen actually were. Not only did nitrogen outperform helium with shorter analysis times, the elution order, peak shapes, and separation numbers were all extremely similar to that of helium. This was the case for both the temperature programming and isothermal experimental conditions. The Van Deemter curves also showed that the optimum velocities between the gases are not as dissimilar as originally thought. It also shows the superiority of nitrogen to the Van Deemter equation. This shows the versatility of nitrogen and the flexibility of its operating conditions. Despite how the alkanes were chosen to be run in the instrument, nitrogen was able to separate them efficiently. Overall, the nitrogen and helium alkane analyses were easily compared to one another and demonstrated how nitrogen can successfully be used to separate these compounds while replacing helium.

Another reason why nitrogen should be considered a reasonable carrier gas alternative was because of the standard test mixtures that were evaluated in this research. Two different complex solutions containing 13-17 chemicals were tested with the different gases. For the Grob test mixture, the separation numbers were, once again, comparable. The values were very close to one another with

a few being almost identical. It was also seen that the nitrogen carrier gas was able to more efficiently elute the compounds as there were more smaller peaks seen close to the baseline that were not seen with the helium separations. This is beneficial because any impurities or degradation of the solution was shown with the nitrogen but not with the helium. Furthermore, the PAH mixture also showed how superior nitrogen can be. The retention times were shorter for all 16 components of the mixture and the separation numbers were extremely close. The critical region was also expanded and analyzed to see which gas was really the most effective. The resolution of the critical pair was higher for nitrogen for both critical pairs tested. This is another reason why nitrogen should be considered an effective carrier gas replacement for helium.

Lastly, an essential oil analysis was also completed in order to test another group of chemicals with the new carrier gas. These complex mixtures were natural products compared to the alkanes and prepared test mixtures analyzed previously. Peppermint, lavender, eucalyptus, and patchouli oils all had lower retention times with nitrogen. This was the third time that nitrogen outperformed helium with shorter analysis times throughout this research. The critical regions of both peppermint and patchouli oils were expanded and the resolution between the critical pair was very comparable between both carrier gases. Like the other experiments, the separation numbers were close and comparable as well. Nitrogen can successfully separate essential oils.

In the end, nitrogen should be considered a practical, effective, and successful alternative carrier gas for the replacement of helium. It was able to separate alkanes, essential oils, and two complex test mixtures similar too, if not better, then helium. It proved to have flexible operating conditions and can be efficient for a variety of chemicals. Nitrogen is a great option for gas chromatography.

### *5. Future Work*

In the future, more gas chromatography testing can be done with a larger variety of chemicals. More natural products, pesticides, polychlorinated biphenyls (PCB's), or environmental compounds can be analyzed to see how those separations compare with the two different carrier gases. The study can be extended further by branching into the forensics or pharmaceutical fields. Testing of compounds such as drugs or biological specimens can be done to see how well nitrogen can perform. Furthermore, a statistical analysis of the Van Deemter curves in terms of linear regression or residual plots can help get a better idea of the performance of nitrogen. If nitrogen is deemed effective in these areas too, then this carrier gas can be implemented in all fields of science. Industries such as flavor and fragrances, forensics, environmental monitoring, pesticide detection, pharmaceuticals, and more can all benefit from nitrogen as helium becomes more limited.

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## *7. Appendix*

### *7.1 Raw Data for $C_6$-$C_{20}$ Analysis*

| **Table 11: Rate: 3°C/min Helium (trial #1, trial #2, trial #3)** | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$(min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.78, 1.78, 1.78 | 0.022, 0.022, 0.022 | --- | --- |
| $C_7$ | 2.10, 2.10, 2.10 | 0.021, 0.022, 0.022 | 6.42, 6.25, 6.25 | 0.080 |
| $C_8$ | 2.75, 2.75, 2.75 | 0.024, 0.024, 0.024 | 13.4, 13.1, 13.1 | 0.132 |
| $C_9$ | 3.99, 3.99, 3.99 | 0.032, 0.032, 0.032 | 21.2, 21.2, 21.2 | 0.019 |
| $C_{10}$ | 6.11, 6.11, 6.10 | 0.047, 0.047, 0.047 | 25.8, 25.7, 25.7 | 0.040 |
| $C_{11}$ | 9.16, 9,15, 9.14 | 0.064, 0.064, 0.064 | 26.5, 26.4, 26.4 | 0.054 |
| $C_{12}$ | 12.9, 12.8, 12.8 | 0.075, 0.076, 0.079 | 26.0, 25.7, 25.1 | 0.354 |
| $C_{13}$ | 17.0, 16.9, 16.9 | 0.087, 0.086, 0.087 | 24.2, 24.2, 23.6 | 0.300 |
| $C_{14}$ | 21.1, 21.1, 21.1 | 0.094, 0.091, 0.092 | 21.9, 22.4, 22.1 | 0.193 |
| $C_{15}$ | 25.2, 25.1, 25.1 | 0.095, 0.094, 0.101 | 20.5, 20.9, 20.0 | 0.372 |
| $C_{16}$ | 29.1, 29.1, 29.1 | 0.105, 0.106, 0.102 | 18.6, 18.6, 18.3 | 0.146 |
| $C_{17}$ | 32.9, 32.8, 32.8 | 0.103, 0.104, 0.098 | 16.9, 16.7, 17.6 | 0.374 |
| $C_{18}$ | 36.5, 36.4, 36.4 | 0.106, 0.111, 0.103 | 16.2, 15.7, 16.8 | 0.468 |
| $C_{19}$ | 39.9, 39.8, 39.8 | 0.123, 0.127, 0.127 | 14.1, 13.5, 14.0 | 0.266 |
| $C_{20}$ | 43.2, 43.1, 43.1 | 0.116, 0.121, 0.114 | 12.5, 12.0, 12.4 | 0.218 |

| **Table 12: Rate: 5°C/min Helium (trial #1, trial #2, trial #3)** | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$(min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.77, 1.77, 1.77 | 0.023, 0.023, 0.022 | --- | --- |
| $C_7$ | 2.07, 2.07, 2.07 | 0.021, 0.021, 0.021 | 5.93, 5.77, 5.77 | 0.075 |
| $C_8$ | 2.65, 2.65, 2.65 | 0.023, 0.023, 0.023 | 12.2, 12.2, 12.2 | 0.000 |
| $C_9$ | 3.70, 3.70, 3.70 | 0.028, 0.028, 0.029 | 19.1, 19.5, 19.5 | 0.189 |
| $C_{10}$ | 5.33, 5.33, 5.33 | 0.038, 0.037, 0.037 | 23.7, 23.8, 24.2 | 0.191 |
| $C_{11}$ | 7.50, 7.50, 7.50 | 0.048, 0.046, 0.048 | 24.5, 24.2, 25.1 | 0.378 |
| $C_{12}$ | 9.99, 9.99, 9.99 | 0.055, 0.054, 0.052 | 23.9, 23.1, 23.9 | 0.349 |
| $C_{13}$ | 12.5, 12.5, 12.6 | 0.058, 0.057, 0.060 | 22.2, 22.0, 22.4 | 0.163 |
| $C_{14}$ | 15.1, 15.1, 15.1 | 0.063, 0.060, 0.061 | 20.3, 20.3, 21.0 | 0.344 |
| $C_{15}$ | 17.6, 17.6, 17.6 | 0.063, 0.065, 0.061 | 19.4, 18.7, 18.9 | 0.285 |
| $C_{16}$ | 20.0, 20.0, 20.0 | 0.069, 0.067, 0.069 | 17.4, 17.1, 17.1 | 0.137 |
| $C_{17}$ | 22.3, 22.3, 23.3 | 0.065, 0.067, 0.067 | 15.7, 15.9, 15.9 | 0.118 |
| $C_{18}$ | 24.5, 24.5, 24.5 | 0.067, 0.072, 0.074 | 14.5, 15.5, 14.7 | 0.446 |
| $C_{19}$ | 26.6, 26.6, 26.6 | 0.083, 0.084, 0.082 | 12.4, 12.9, 12.4 | 0.250 |
| $C_{20}$ | 28.5, 28.5, 28.5 | 0.079, 0.080, 0.074 | 11.6, 11.1, 10.9 | 0.261 |

| Table 13: Rate: 8°C/min Helium (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.75, 1.75, 1.75 | 0.024, 0.023, 0.023 | --- | --- |
| $C_7$ | 2.02, 2.02, 2.02 | 0.021, 0.021, 0.021 | 5.00, 5.16, 5.16 | 0.075 |
| $C_8$ | 2.52, 2.52, 2.52 | 0.022, 0.022, 0.021 | 10.6, 10.6, 10.9 | 0.132 |
| $C_9$ | 3.37, 3.37, 3.37 | 0.026, 0.025, 0.025 | 16.7, 17.1, 17.4 | 0.311 |
| $C_{10}$ | 4.60, 4.60, 4.60 | 0.031, 0.031, 0.031 | 20.6, 20.9, 20.9 | 0.172 |
| $C_{11}$ | 6.12, 6.12, 6.12 | 0.037, 0.037, 0.036 | 21.4, 22.3, 21.2 | 0.158 |
| $C_{12}$ | 7.79, 7.79, 7.79 | 0.040, 0.039, 0.040 | 20.6, 20.9, 20.2 | 0.130 |
| $C_{13}$ | 9.48, 9.48, 9.48 | 0.042, 0.042, 0.040 | 19.6, 19.9, 20.1 | 0.208 |
| $C_{14}$ | 11.1, 11.1, 11.1 | 0.044, 0.043, 0.043 | 18.2, 18.4, 18.9 | 0.283 |
| $C_{15}$ | 12.7, 12.7, 12.7 | 0.046, 0.045, 0.044 | 16.6, 17.0, 17.2 | 0.252 |
| $C_{16}$ | 14.2, 14.2, 14.2 | 0.048, 0.046, 0.049 | 15.1, 15.7, 15.3 | 0.228 |
| $C_{17}$ | 15.6, 15.6, 15.6 | 0.047, 0.043, 0.044 | 14.1, 15.1, 14.4 | 0.416 |
| $C_{18}$ | 17.0, 17.0, 17.0 | 0.050, 0.051, 0.051 | 13.2, 13.7, 13.5 | 0.188 |
| $C_{19}$ | 18.4, 18.4, 18.4 | 0.058, 0.061, 0.059 | 11.3, 10.8, 11.0 | 0.176 |
| $C_{20}$ | 19.6, 19.6, 19.6 | 0.054, 0.054, 0.054 | 10.0, 9.78, 9.99 | 0.129 |

| Table 14: Rate: 10°C/min Helium (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.74, 1.74, 1.74 | 0.024, 0.024, 0.024 | --- | --- |
| $C_7$ | 2.00, 2.00, 2.00 | 0.021, 0.021, 0.021 | 4.67, 4.64, 4.64 | 0.014 |
| $C_8$ | 2.46, 2.46, 2.46 | 0.021, 0.021, 0.021 | 9.93, 9.93, 9.93 | 0.000 |
| $C_9$ | 3.21, 3.21, 3.21 | 0.023, 0.023, 0.024 | 16.1, 16.1, 15.7 | 0.179 |
| $C_{10}$ | 4.27, 4.21, 4.27 | 0.028, 0.028, 0.028 | 19.7, 19.7, 19.3 | 0.193 |
| $C_{11}$ | 5.54, 5.54, 5.54 | 0.032, 0.031, 0.031 | 20.5, 20.1, 20.4 | 0.172 |
| $C_{12}$ | 6.90, 6.90, 6.90 | 0.035, 0.034, 0.035 | 20.0, 19.3, 19.0 | 0.261 |
| $C_{13}$ | 8.28, 8.28, 8.28 | 0.037, 0.036, 0.037 | 18.6, 18.1, 18.1 | 0.255 |
| $C_{14}$ | 9.62, 9.62, 9.62 | 0.038, 0.037, 0.038 | 17.3, 16.8, 16.8 | 0.231 |
| $C_{15}$ | 10.9, 10.9, 10.9 | 0.040, 0.039, 0.039 | 15.9, 15.4, 15.6 | 0.214 |
| $C_{16}$ | 12.1, 12.1, 12.1 | 0.042, 0.041, 0.040 | 14.3, 13.9, 14.5 | 0.235 |
| $C_{17}$ | 13.2, 13.2, 13.2 | 0.039, 0.041, 0.038 | 13.1, 13.3, 13.8 | 0.298 |
| $C_{18}$ | 14.3, 14.3, 14.4 | 0.041, 0.042, 0.043 | 12.4, 12.9, 12.7 | 0.208 |
| $C_{19}$ | 15.4, 15.4, 15.4 | 0.049, 0.049, 0.048 | 10.7, 10.8, 10.7 | 0.061 |
| $C_{20}$ | 16.4, 16.4, 16.4 | 0.046, 0.045, 0.044 | 9.60, 9.52, 9.86 | 0.142 |

| Table 15: Rate: 13°C/min Helium (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$(min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.73, 1.73, 1.73 | 0.024, 0.024, 0.024 | --- | --- |
| $C_7$ | 1.96, 1.96, 1.96 | 0.020, 0.020, 0.021 | 4.30, 4.30, 4.17 | 0.061 |
| $C_8$ | 2.37, 2.37, 2.37 | 0.021, 0.021, 0.021 | 8.93, 8.93, 8.69 | 0.113 |
| $C_9$ | 3.01, 3.02, 3.02 | 0.023, 0.023, 0.023 | 13.6, 13.6, 13.6 | 0.009 |
| $C_{10}$ | 3.89, 3.89, 3.89 | 0.025, 0.026, 0.026 | 17.7, 16.8, 16.0 | 0.174 |
| $C_{11}$ | 4.91, 4.91, 4.91 | 0.028, 0.028, 0.028 | 18.2, 17.8, 17.9 | 0.174 |
| $C_{12}$ | 5.98, 5.98, 5.98 | 0.030, 0.030, 0.030 | 17.5, 17.5, 17.5 | 0.000 |
| $C_{13}$ | 7.06, 7.06, 7.06 | 0.031, 0.030, 0.031 | 16.6, 16.9, 16.6 | 0.137 |
| $C_{14}$ | 8.10, 8.10, 8.10 | 0.032, 0.032, 0.032 | 15.5, 15.7, 15.5 | 0.118 |
| $C_{15}$ | 9.10, 9.09, 9.09 | 0.033, 0.032, 0.033 | 14.3, 14.5, 14.2 | 0.116 |
| $C_{16}$ | 10.0, 10.0, 10.0 | 0.035, 0.034, 0.035 | 12.9, 13.3, 12.9 | 0.196 |
| $C_{17}$ | 10.9, 10.9, 10.9 | 0.033, 0.033, 0.033 | 12.1, 12.3, 12.1 | 0.094 |
| $C_{18}$ | 11.8, 11.8, 11.8 | 0.037, 0.036, 0.036 | 11.3, 11.4, 11.4 | 0.085 |
| $C_{19}$ | 12.6, 12.6, 12.6 | 0.040, 0.040, 0.040 | 9.74, 9.89, 9.88 | 0.068 |
| $C_{20}$ | 13.4, 13.4, 13.4 | 0.037, 0.038, 0.038 | 9.03, 8.88, 8.90 | 0.066 |

| Table 16: Rate: 15°C/min Helium (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$(min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.72, 1.72, 1.72 | 0.024, 0.024, 0.024 | --- | --- |
| $C_7$ | 1.94, 1.94, 1.94 | 0.020, 0.020, 0.020 | 4.05, 4.05, 4.02 | 0.014 |
| $C_8$ | 2.32, 2.34, 2.32 | 0.020, 0.020, 0.020 | 8.45, 8.45, 8.48 | 0.014 |
| $C_9$ | 2.91, 2.91, 2,91 | 0.021, 0.021, 0.021 | 13.3, 13.3, 13.3 | 0.000 |
| $C_{10}$ | 3.69, 3.69, 3.69 | 0.024, 0.024, 0.024 | 16.3, 16.3, 16.3 | 0.009 |
| $C_{11}$ | 4.59, 4.59, 4.59 | 0.026, 0.027, 0.026 | 16.6, 17.0, 17.0 | 0.170 |
| $C_{12}$ | 5.54, 5.54, 5.54 | 0.028, 0.027, 0.028 | 16.4, 16.4, 16.4 | 0.009 |
| $C_{13}$ | 6.48, 6.48, 6.48 | 0.029, 0.028, 0.030 | 16.0, 15.1, 15.4 | 0.359 |
| $C_{14}$ | 7.38, 7.38, 7.38 | 0.030, 0.030, 0.029 | 14.4, 14.3, 14.3 | 0.130 |
| $C_{15}$ | 8.25, 8.25, 8.25 | 0.030, 0.031, 0.030 | 13.1, 13.6, 13.4 | 0.204 |
| $C_{16}$ | 9.07, 9.07, 9.07 | 0.031, 0.032, 0.031 | 12.1, 12.5, 12.5 | 0.198 |
| $C_{17}$ | 9.86, 9.85, 9.85 | 0.031, 0.030, 0.030 | 11.5, 11.7, 11.6 | 0.100 |
| $C_{18}$ | 10.6, 10.6, 10.6 | 0.032, 0.032, 0.033 | 11.1, 10.8, 10.8 | 0.099 |
| $C_{19}$ | 11.3, 11.3, 11.3 | 0.037, 0.036, 0.036 | 9.57, 9.42, 9.42 | 0.071 |
| $C_{20}$ | 12.0, 11.9, 11.9 | 0.034, 0.034, 0.034 | 8.60, 8.60, 8.46 | 0.066 |

| Table 17: Rate: 20°C/min Helium (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.71, 1.71, 1.71 | 0.025, 0.025, 0.024 | --- | --- |
| $C_7$ | 1.90, 1.90, 1.90 | 0.021, 0.020, 0.020 | 3.24, 3.33, 3.43 | 0.078 |
| $C_8$ | 2.22, 2.22, 2.22 | 0.020, 0.020, 0.020 | 6.80, 7.00, 7.00 | 0.094 |
| $C_9$ | 2.70, 2.70, 2.70 | 0.020, 0.020, 0.020 | 11.0, 11.0, 11.0 | 0.000 |
| $C_{10}$ | 3.33, 3.32, 3.32 | 0.022,0.022, 0.022 | 13.7, 13.7, 13.7 | 0.014 |
| $C_{11}$ | 4.02, 4.02, 4.02, | 0.024, 0.024, 0.024 | 14.2, 14.2, 14.2 | 0.000 |
| $C_{12}$ | 4.75, 4.71, 4.72 | 0.025, 0.025, 0.025 | 13.7, 13.7, 13.7 | 0.021 |
| $C_{13}$ | 5.46, 5.43, 5.44 | 0.025, 0.025, 0.025 | 13.2, 13.2, 13.2 | 0.009 |
| $C_{14}$ | 6.15, 6.11, 6.15 | 0.027, 0.027, 0.026 | 12.2, 12.2, 12.4 | 0.128 |
| $C_{15}$ | 6.80, 6.85, 6.80 | 0.026, 0.026, 0.026 | 11.3, 11.3, 11.5 | 0.109 |
| $C_{16}$ | 7.43, 7.40, 7.43 | 0.028, 0.028, 0.027 | 10.5, 10.5, 10.7 | 0.106 |
| $C_{17}$ | 8.02, 8.01, 8.02 | 0.027, 0.027, 0.026 | 9.73, 9.71, 10.1 | 0.184 |
| $C_{18}$ | 8.58, 8.58, 8.58 | 0.028, 0.028, 0.027 | 9.27, 9.29, 9.68 | 0.189 |
| $C_{19}$ | 9.13, 9.13, 9.13 | 0.033, 0.033, 0.032 | 7.98, 8.00, 8.29 | 0.142 |
| $C_{20}$ | 9.69, 9.70, 9.69 | 0.033, 0.032, 0.033 | 7.58, 7.71, 7.69 | 0.057 |

| Table 18: Rate: 3°C/min Nitrogen (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.63, 1.63, 1.63 | 0.031, 0.031, 0.030 | --- | --- |
| $C_7$ | 1.92, 1.92, 1.92 | 0.031, 0.030, 0.030 | 3.66, 3.88, 3.80 | 0.091 |
| $C_8$ | 2.50, 2.51, 2.51 | 0.031, 0.030, 0.030 | 8.26, 8.73, 8.82 | 0.246 |
| $C_9$ | 3.63, 3.64, 3.64 | 0.036, 0.037, 0.037 | 15.7, 15.8, 15.8 | 0.032 |
| $C_{10}$ | 5.57, 5.58, 5.58 | 0.051, 0.051, 0.050 | 21.3, 21.1, 21.3 | 0.123 |
| $C_{11}$ | 8.44, 8.46, 8.46 | 0.068, 0.068, 0.069 | 22.1, 23.1, 23.1 | 0.014 |
| $C_{12}$ | 12.0, 12.0, 12.0 | 0.083, 0.081, 0.083 | 22.9,23.2, 22.7 | 0.205 |
| $C_{13}$ | 16.0, 16.0, 16.0 | 0.092, 0.095, 0.096 | 21.8, 21.7, 21.3 | 0.222 |
| $C_{14}$ | 20.1, 20.1, 20.1 | 0.101, 0.103, 0.096 | 20.2, 19.6, 20.3 | 0.290 |
| $C_{15}$ | 24.1, 24.2, 24.2 | 0.102, 0.102, 0.100 | 18.8, 18.6, 19.5 | 0.384 |
| $C_{16}$ | 28.0, 28.1, 28.1 | 0.109, 0.113, 0.108 | 17.5, 17.1, 17.7 | 0.263 |
| $C_{17}$ | 31.8, 31.8, 31.8 | 0.111, 0.106, 0.111 | 15.8, 15.9, 15.9 | 0.031 |
| $C_{18}$ | 35.3, 35.3, 35.3 | 0.116, 0.118, 0.117 | 14.7, 14.9, 14.6 | 0.125 |
| $C_{19}$ | 38.8, 38.8, 38.8 | 0.128, 0.130, 0.128 | 13.1, 12.8, 13.0 | 0.107 |
| $C_{20}$ | 42.0, 42.0, 42.0 | 0.119, 0.120,0.119 | 12.0, 11.9, 12.0 | 0.066 |

| Table 19: Rate: 5°C/min Nitrogen (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths(min) | SN | SD |
| $C_6$ | 1.62, 1.62, 1.62 | 0.029, 0.030, 0.030 | --- | --- |
| $C_7$ | 1.89, 1.89, 1.89 | 0.028, 0.029, 0.029 | 3.77, 3.61, 3.61 | 0.075 |
| $C_8$ | 2.42, 2.42, 2.42 | 0.028, 0.028, 0.028 | 8.45, 8.28, 8.26 | 0.085 |
| $C_9$ | 3.38, 3.38, 3.38 | 0.032, 0.032, 0.032 | 15.0, 15.0, 15.0 | 0.000 |
| $C_{10}$ | 4.91, 4.91, 4.91 | 0.041, 0.041, 0.041 | 19.9, 19.9, 19.9 | 0.005 |
| $C_{11}$ | 6.99, 6.99, 6.99 | 0.051, 0.051, 0.051 | 21.5, 21.5, 21.5 | 0.005 |
| $C_{12}$ | 9.41, 9.41, 9.41 | 0.059, 0.057, 0.058 | 21.0, 21.2, 21.4 | 0.163 |
| $C_{13}$ | 11.9, 11.9, 11.9 | 0.064, 0.064, 0.062 | 19.8, 20.3, 20.1 | 0.216 |
| $C_{14}$ | 14.5, 14.5, 14.5 | 0.067, 0.066, 0.065 | 18.5, 19.1, 18.6 | 0.253 |
| $C_{15}$ | 17.0, 17.0, 17.0 | 0.071, 0.068, 0.067 | 16.9, 17.7, 17.5 | 0.341 |
| $C_{16}$ | 19.4, 19.3, 19.3 | 0.071, 0.072, 0.074 | 15.8, 15.9, 16.0 | 0.096 |
| $C_{17}$ | 21.6, 21.6, 21.6 | 0.071, 0.069, 0.069 | 14.9, 14.8, 15.0 | 0.102 |
| $C_{18}$ | 23.8, 23.8, 23.8 | 0.078, 0.078, 0.076 | 13.6, 14.0, 13.8 | 0.163 |
| $C_{19}$ | 25.9, 25.9, 25.9 | 0.084, 0.086, 0.085 | 11.9, 12.0, 11.7 | 0.104 |
| $C_{20}$ | 27.8, 27.9, 27.8 | 0.080, 0.080, 0.078 | 10.9, 11.0, 10.8 | 0.090 |

| Table 20: Rate: 8°C/min Nitrogen (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths (min) | SN | SD |
| $C_6$ | 1.60, 1.61, 1.60 | 0.030, 0.031, 0.031 | --- | --- |
| $C_7$ | 1.85, 1.85, 1.85 | 0.029, 0.030, 0.029 | 3.15, 3.07, 3.20 | 0.054 |
| $C_8$ | 2.31, 2.31, 2.31 | 0.027, 0.027, 0.027 | 7.20, 7.07, 7.21 | 0.064 |
| $C_9$ | 3.10, 3.10, 3.10 | 0.029, 0.030, 0.029 | 13.0, 12.7, 13.0 | 0.116 |
| $C_{10}$ | 4.26, 4.26, 4.27 | 0.033, 0.034, 0.034 | 17.4, 17.1, 17.7 | 0.245 |
| $C_{11}$ | 5.73, 5.73, 5.76 | 0.039, 0.039, 0.038 | 19.3, 19.1, 19.3 | 0.127 |
| $C_{12}$ | 7.36, 7.36, 7.36 | 0.042, 0.043, 0.043 | 19.1, 18.8, 19.1 | 0.121 |
| $C_{13}$ | 9.03, 9.03, 9.03 | 0.045, 0.045, 0.047 | 17.5, 17.9, 18.2 | 0.260 |
| $C_{14}$ | 10.6, 10.6, 10.6 | 0.048, 0.047, 0.048 | 16.2, 16.8, 16.6 | 0.235 |
| $C_{15}$ | 12.2, 12.2, 12.2 | 0.048, 0.048, 0.048 | 15.4, 15.6, 15.6 | 0.083 |
| $C_{16}$ | 13.7, 13.7, 13.7 | 0.051, 0.050, 0.051 | 14.3, 14.4, 14.4 | 0.066 |
| $C_{17}$ | 15.2, 15.2, 15.2 | 0.050, 0.050, 0.050 | 13.2, 13.3, 13.2 | 0.073 |
| $C_{18}$ | 16.5, 16.5, 16.5 | 0.051, 0.054, 0.054 | 12.2, 12.2, 12.6 | 0.177 |
| $C_{19}$ | 17.9, 17.9, 17.9 | 0.060, 0.060, 0.060 | 10.6, 10.6, 10.9 | 0.156 |
| $C_{20}$ | 19.1, 19.1, 19.1 | 0.057, 0.056, 0.054 | 9.88, 9.72, 9.61 | 0.111 |

| Table 21: Rate: 10°C/min Nitrogen (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths (min) | SN | SD |
| $C_6$ | 1.59, 1.59, 1.60 | 0.028, 0.031, 0.028 | --- | --- |
| $C_7$ | 1.83, 1.83, 1.83 | 0.026, 0.028, 0.026 | 2.97, 3.33, 3.33 | 0.170 |
| $C_8$ | 2.25, 2.25, 2.25 | 0.026, 0.025, 0.025 | 6.94, 7.29, 7.10 | 0.143 |
| $C_9$ | 2.95, 2.95, 2.95 | 0.026, 0.027, 0.026 | 12.5, 12.7, 12.5 | 0.118 |
| $C_{10}$ | 3.96, 3.96, 3.96 | 0.031, 0.030, 0.030 | 16.6, 16.9, 16.5 | 0.146 |
| $C_{11}$ | 5.19, 5.19, 5.19 | 0.034, 0.034, 0.034 | 18.2, 18.2, 17.9 | 0.134 |
| $C_{12}$ | 6.53, 6.53, 6.53 | 0.037, 0.037, 0.037 | 17.8, 17.8, 17.8 | 0.009 |
| $C_{13}$ | 7.89, 7.89, 7.89 | 0.039, 0.039, 0.039 | 16.8, 16.8, 16.8 | 0.008 |
| $C_{14}$ | 9.22, 9.22, 9.22 | 0.040, 0.040, 0.041 | 15.8, 15.6, 15.2 | 0.099 |
| $C_{15}$ | 10.4, 10.4, 10.4 | 0.042, 0.040, 0.040 | 14.9, 14.7, 14.5 | 0.159 |
| $C_{16}$ | 11.7, 11.7, 11.7 | 0.044, 0.043, 0.044 | 13.7, 13.5, 13.2 | 0.208 |
| $C_{17}$ | 12.8, 12.8, 12.8 | 0.042, 0.044, 0.043 | 12.2, 12.2, 12.4 | 0.073 |
| $C_{18}$ | 13.9, 13.9, 13.9 | 0.045, 0.046, 0.044 | 11.3, 11.7, 11.7 | 0.193 |
| $C_{19}$ | 15.0, 15.0, 15.0 | 0.050, 0.049, 0.051 | 10.2, 10.2, 11.2 | 0.016 |
| $C_{20}$ | 16.0, 16.0, 16.0 | 0.048, 0.047, 0.048 | 9.42, 9.08, 9.20 | 0.141 |

| Table 22: Rate: 13°C/min Nitrogen (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths (min) | SN | SD |
| $C_6$ | 1.59, 1.59, 1.59 | 0.030, 0.031, 0.030 | --- | --- |
| $C_7$ | 1.80, 1.80, 1.80 | 0.028, 0.028, 0.029 | 2.69, 2.60, 2.66 | 0.037 |
| $C_8$ | 2.18, 2.17, 2.18 | 0.025,0.025, 0.026 | 6.08, 5.84, 6.11 | 0.121 |
| $C_9$ | 2.78, 2.78, 2.78 | 0.025, 0.026, 0.025 | 10.8, 10.8, 11.0 | 0.109 |
| $C_{10}$ | 3.62, 3.61, 3.62 | 0.028, 0.028, 0.028 | 14.4, 14.2, 14.7 | 0.118 |
| $C_{11}$ | 4.61, 4.61, 4.61 | 0.029, 0.030, 0.030 | 16.1, 16.1, 16.3 | 0.119 |
| $C_{12}$ | 5.67, 5.67, 5.67 | 0.032, 0.032, 0.032 | 16.1, 16.0, 16.3 | 0.126 |
| $C_{13}$ | 6.73, 6.74, 6.73 | 0.034, 0.033, 0.033 | 15.4, 15.3, 15.1 | 0.130 |
| $C_{14}$ | 7.76, 7.77, 7.76 | 0.034, 0.034, 0.035 | 14.4, 14.1, 14.1 | 0.123 |
| $C_{15}$ | 8.75, 8.76, 8.75 | 0.035, 0.035, 0.035 | 13.3, 13.1, 13.3 | 0.106 |
| $C_{16}$ | 9.70, 9.71, 9.70 | 0.037, 0.036, 0.037 | 12.3, 12.1, 12.1 | 0.090 |
| $C_{17}$ | 10.6, 10.6, 10.6 | 0.036, 0.036, 0.036 | 11.4, 11.2, 11.2 | 0.083 |
| $C_{18}$ | 11.4, 11.4, 11.4 | 0.038, 0.037, 0.040 | 10.7, 10.3, 10.6 | 0.187 |
| $C_{19}$ | 12.2, 12.3, 12.2 | 0.043, 0.043, 0.042 | 9.35, 9.07, 9.21 | 0.114 |
| $C_{20}$ | 13.0, 13.0, 13.0 | 0.040, 0.041, 0.041 | 8.21, 8.33, 8.31 | 0.052 |

| Table 23: Rate: 15°C/min Nitrogen (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths (min) | SN | SD |
| $C_6$ | 1.58, 1.58, 1.58 | 0.031, 0.030, 0.030 | --- | --- |
| $C_7$ | 1.79, 1.79, 1.79 | 0.029, 0.028, 0.028 | 2.55, 2.53, 3.42 | 0.057 |
| $C_8$ | 2.14, 2.14, 2.14 | 0.025, 0.024, 0.024 | 5.73, 5.75, 5.50 | 0.113 |
| $C_9$ | 2.69, 2.69, 2.69 | 0.025, 0.024, 0.024 | 10.4, 10.5, 10.0 | 0.226 |
| $C_{10}$ | 3.44, 3.44, 3.44 | 0.026, 0.026, 0.026 | 13.9, 13.9, 13.9 | 0.127 |
| $C_{11}$ | 4.32, 4.32, 4.32 | 0.028, 0.028, 0.028 | 15.2, 15.2, 15.2 | 0.009 |
| $C_{12}$ | 5.24, 5.24, 5.25 | 0.030, 0.030, 0.029 | 15.0, 15.3, 15.0 | 0.129 |
| $C_{13}$ | 6.17, 1.97, 6.17 | 0.031, 0.030, 0.031 | 14.4, 14.4, 14.2 | 0.127 |
| $C_{14}$ | 7.07, 7.07, 7.07 | 0.032, 0.032, 0.032 | 13.5, 13.3, 13.3 | 0.108 |
| $C_{15}$ | 7.94, 7.94, 7.94 | 0.032, 0.032, 0.032, | 12.4, 12.4, 12.4 | 0.005 |
| $C_{16}$ | 8.76, 8.76, 8.76 | 0.034, 0.033, 0.034 | 11.6, 11.5, 11.4 | 0.095 |
| $C_{17}$ | 9.54, 9.54, 9.54 | 0.033, 0.034, 0.032 | 10.6, 10.7, 10.3 | 0.075 |
| $C_{18}$ | 10.2, 10.2, 10.2 | 0.034, 0.034, 0.034 | 10.0, 10.3, 10.1 | 0.143 |
| $C_{19}$ | 11.0, 11.0, 11.0 | 0.040, 0.039, 0.039 | 8.86, 8.85, 8.73 | 0.059 |
| $C_{20}$ | 11.6, 11.6, 11.6 | 0.037, 0.037, 0.037 | 7.84, 7.86, 7.74 | 0.052 |

| Table 24: Rate: 20°C/min Nitrogen (trial #1, trial #2, trial #3) | | | | |
|---|---|---|---|---|
| Carbon # | $t_R$ (min) | Peak widths (min) | SN | SD |
| $C_6$ | 1.57, 1.57, 1.57 | 0.030, 0.031, 0.031 | --- | --- |
| $C_7$ | 1.75, 1.73, 1.75 | 0.027, 0.028, 0.027 | 2.10, 2.19, 2.16 | 0.037 |
| $C_8$ | 2.05, 2.05, 2.05 | 0.024, 0.024, 0.023 | 4.75, 4.90, 4.96 | 0.088 |
| $C_9$ | 2.50, 2.50, 2.50 | 0.022, 0.023, 0.022 | 8.70, 8.89, 9.15 | 0.184 |
| $C_{10}$ | 3.10, 3.10, 3.10 | 0.024, 0.024, 0.024 | 11.6, 11.9, 11.9 | 0.141 |
| $C_{11}$ | 3.78, 3.78, 3.78 | 0.025, 0.025, 0.025 | 12.9, 12.9, 12.9 | 0.000 |
| $C_{12}$ | 4.49, 4.49, 4.49 | 0.025, 0.026, 0.026 | 12.9, 13.2, 12.9 | 0.118 |
| $C_{13}$ | 5.20, 5.20, 5.20 | 0.027, 0.026, 0.027 | 12.5, 12.5, 12.3 | 0.123 |
| $C_{14}$ | 5.88, 5.88, 5.88 | 0.027, 0.027, 0.027 | 11.8, 11.6, 11.6 | 0.109 |
| $C_{15}$ | 6.53, 6.54, 6.54 | 0.028, 0.027, 0.027 | 11.0, 10.8, 11.0 | 0.099 |
| $C_{16}$ | 7.16, 7.16, 7.16 | 0.029, 0.029, 0.029 | 10.1, 9.93, 10.1 | 0.097 |
| $C_{17}$ | 7.71, 7.75, 7.75 | 0.028, 0.028, 0.028 | 9.33, 9.33, 9.33 | 0.000 |
| $C_{18}$ | 8.31, 8.31, 8.31 | 0.029, 0.029, 0.029 | 8.93, 8.93, 8.93 | 0.000 |
| $C_{19}$ | 8.81, 8.86, 8.86 | 0.032, 0.032, 0.033 | 7.93, 7.92, 7.79 | 0.064 |
| $C_{20}$ | 9.35, 9.39, 9.39 | 0.033, 0.032, 0.033 | 7.33, 7.22, 7.08 | 0.102 |

### *7.2 Raw Data for $C_{14}$ Analysis*

| Table 25: Helium Trials | | | |
|---|---|---|---|
| Pressure | $t_M$ (min) | $t_R$ (min) | Peak widths for $t_M$ and $t_R$ (min) |
| 30 psi | 1.11 | 9.22 | 0.037, 0.341 |
| 40 psi | 0.862 | 7.08 | 0.030, 0.262 |
| 50 psi | 0.710 | 5.77 | 0.027, 0.212 |
| 60 psi | 0.609 | 4.88 | 0.025, 0.178 |
| 70 psi | 0.529 | 4.24 | 0.022, 0.156 |
| 80 psi | 0.471 | 3.75 | 0.021, 0.140 |
| 90 psi | 0.428 | 3.36 | 0.022, 0.127 |
| 100 psi | 0.388 | 3.05 | 0.020, 0.116 |
| 110 psi | 0.356 | 2.79 | 0.019, 0.108 |
| 120 psi | 0.334 | 2.58 | 0.021, 0.101 |
| 130 psi | 0.311 | 2.38 | 0.020, 0.095 |

| Table 26: Nitrogen Trials | | | |
|---|---|---|---|
| Pressure | $t_M$ (min) | $t_R$ (min) | Peak widths for $t_M$ and $t_R$ (min) |
| 30 psi | 1.02 | 8.14 | 0.036, 0.287 |
| 40 psi | 0.795 | 6.20 | 0.030, 0.223 |
| 50 psi | 0.656 | 5.02 | 0.027, 0.184 |
| 60 psi | 0.566 | 4.22 | 0.026, 0.160 |
| 70 psi | 0.498 | 3.64 | 0.026, 0.143 |
| 80 psi | 0.449 | 3.20 | 0.030, 0.132 |
| 90 psi | 0.407 | 2.85 | 0.031, 0.122 |
| 100 psi | 0.361 | 2.55 | 0.022, 0.111 |
| 110 psi | 0.333 | 2.32 | 0.022, 0.106 |
| 120 psi | 0.308 | 2.12 | 0.022, 0.099 |
| 130 psi | 0.287 | 1.95 | 0.021, 0.096 |

| Table 27: Column Length | |
|---|---|
| Pressure (psi) | Column Length (cm) |
| 30 psi | 3000cm |
| 40 psi | 3000cm |
| 50 psi | 3000 cm |
| 60 psi | 3000 cm |
| 70 psi | 3000 cm |
| 80 psi | 3000 cm |
| 90 psi | 3000 cm |
| 100 psi | 3000 cm |
| 110 psi | 3000 cm |
| 120 psi | 3000 cm |
| 130 psi | 3000cm |

### *7.3 Raw Data for the Grob Test Mixture Analysis*

| **Table 28: Helium 50:1 Split Ratio (trial #1, trial #2, trial #3)** | | |
|---|---|---|
| Peak # | $t_R$ (min) | Peak widths (min) |
| 1 | 1.92, 1.55, 1.55 | 0.031, 0.030, 0.038 |
| 2 | 3.23, 2.70, 2.71 | 0.022, 0.022, 0.024 |
| 3 | 3.33, 2.79, 2.79 | 0.021, 0.022, 0.023 |
| 4 | 6.13, 5.44, 5.45 | 0.024, 0.024, 0.025 |
| 5 | 7.17, 6.46, 6.47 | 0.025, 0.025, 0.026 |
| 6 | 7.65, 6.94, 6.94 | 0.025, 0.025, 0.026 |
| 7 | 7.72, 7.00, 7.00 | 0.025, 0.025, 0.027 |
| 8 | 7.78, 7.05, 7.05 | 0.028, 0.028, 0.031 |
| 9 | 8.72, 7.97, 7.97 | 0.026, 0.025, 0.028 |
| 10 | 10.9, 10.1, 10.1 | 0.026, 0.026, 0.027 |
| 11 | 12.2, 11.5, 11.5 | 0.026, 0.026, 0.027 |
| 12 | 12.3, 11.5, 11.5 | 0.044, 0.044, 0.042 |
| 13 | 13.5, 12.7, 12.7 | 0.027, 0.027, 0.027 |

| **Table 29: Helium 15:1 Split Ratio (trial #1, trial #2, trial #3)** | | |
|---|---|---|
| Peak # | $t_R$ (min) | Peak widths (min) |
| 1 | 1.55, 1.55, 1.55 | 0.045, 0.045, 0.045 |
| 2 | 2.72, 2.72, 2.72 | 0.023, 0.023, 0.023 |
| 3 | 2.81, 2.81, 2.81 | 0.024, 0.024, 0.024 |
| 4 | 5.45, 5.45, 5.45 | 0.024, 0.024, 0.024 |
| 5 | 6.47, 6.47, 6.47 | 0.025, 0.025, 0.026 |
| 6 | 6.94, 6.94, 6.94 | 0.026, 0.026, 0.026 |
| 7 | 7.00, 7.01, 7.01 | 0.025, 0.025, 0.025 |
| 8 | 7.06, 7.06, 7.06 | 0.027, 0.028, 0.028 |
| 9 | 7.97, 7.97, 7.97 | 0.027, 0.026, 0.027 |
| 10 | 10.1, 10.1, 10.1 | 0.026, 0.026, 0.026 |
| 11 | 11.5, 11.5, 11.5 | 0.027, 0.026, 0.027 |
| 12 | 11.6, 11.6, 11.6 | 0.070, 0.069, 0.068 |
| 13 | 12.7, 12.7, 12.7 | 0.027, 0.026, 0.027 |

| Table 30: Nitrogen 50:1 Split Ratio (trial #1, trial #2) | | |
|---|---|---|
| Peak # | $t_R$ (min) | Peak widths (min) |
| 1 | 1.88, 1.88 | 0.042, 0.042 |
| 2 | 3.15, 3.15 | 0.026, 0.026 |
| 3 | 3.25, 3.25 | 0.027, 0.027 |
| 4 | 5.98, 5.98 | 0.029, 0.029 |
| 5 | 7.02, 7.02 | 0.030, 0.030 |
| 6 | 7.49, 7.49 | 0.032, 0.032 |
| 7 | 7.57, 7.57 | 0.030, 0.031 |
| 8 | 7.64, 7.64 | 0.031, 0.031 |
| 9 | 8.57, 8.57 | 0.030, 0.030 |
| 10 | 10.7, 10.7 | 0.032, 0.032 |
| 11 | 12.0, 12.0 | 0.033, 0.032 |
| 12 | 12.2, 12.2 | 0.080, 0.078 |
| 13 | 13.3, 12.3 | 0.033, 0.033 |

| Table 31: Nitrogen 15:1 Split Ratio (trial #1, trial #2) | | |
|---|---|---|
| Peak # | $t_R$ (min) | Peak widths (min) |
| 1 | 1.87, 1.87 | 0.065, 0.065 |
| 2 | 3.18, 3.18 | 0.042, 0.042 |
| 3 | 3.29, 3.28 | 0.040,0.041 |
| 4 | 5.99, 5.99 | 0.030, 0.031 |
| 5 | 7.04, 7.04 | 0.037, 0.037 |
| 6 | 7.50, 7.50 | 0.033, 0.033 |
| 7 | 7.59, 7.59 | 0.039, 0.039 |
| 8 | 7.66, 7.66 | 0.033, 0.033 |
| 9 | 8.58, 8.59 | 0.035, 0.035 |
| 10 | 10.7, 10.7 | 0.034, 0.034 |
| 11 | 12.1, 12.1 | 0.036, 0.034 |
| 12 | 12.2, 12.2 | 0.121, 0.110 |
| 13 | 13.3, 13.3 | 0.037, 0.036 |

**Only 2 trials of nitrogen were completed because leftover Grob test mixture had evaporated**

### *7.4 Raw Data for Essential Oil Analysis*

| **Table 32: Helium (trial #1, trial #2, trial #3)** | | | |
|---|---|---|---|
| Oil | Peak # | $t_R$ (min) | Peak widths (min) |
| Peppermint | 1 | 1.64, 1.64, 1.64 | 0.027, 0.026, 0.027 |
| | 2 | 8.19, 8.19, 8.18 | 0.027, 0.027, 0.027 |
| | 3 | 10.2, 10.2, 10.2 | 0.043, 0.044, 0.046 |
| | 4 | 10.6, 10.6, 10.6 | 0.064, 0.063, 0.063 |
| | 5 | 11.8, 11.8, 11.8 | 0.023, 0.022, 0.023 |
| Lavender | 1 | 1.64, 1.64, 1.64 | 0.031, 0.031, 0.031 |
| | 2 | 9.29, 9.30, 9.30 | 0.064, 0.063, 0.061 |
| | 3 | 11.3, 11.4, 11.4 | 0.041, 0.041, 0.041 |
| Eucalyptus | 1 | 1.63, 1.63, 1.64 | 0.025, 0.025, 0.026 |
| | 2 | 8.27, 8.27, 8.27 | 0.075, 0.075, 0.075 |
| Patchouli | 1 | 1.64, 1.63, 1.64 | 0.031, 0.030, 0.031 |
| | 2 | 12.9, 12.9, 12.9 | 0.021, 0.022, 0.022 |
| | 3 | 13.3, 13.3, 13.3 | 0.023, 0.023, 0.022 |
| | 4 | 14.3, 14.3, 14.3 | 0.026, 0.026, 0.026 |

| **Table 33: Nitrogen (trial #1, trial #2, trial #3)** | | | |
|---|---|---|---|
| Oil | Peak # | $t_R$ (min) | Peak widths (min) |
| Peppermint | 1 | 1.64, 1.64, 1.49 | 0.053, 0.053, 0.053 |
| | 2 | 8.07, 8.06, 7.75 | 0.034, 0.034, 0.038 |
| | 3 | 10.1, 10.1, 9.81 | 0.045, 0.044, 0.047 |
| | 4 | 10.5, 10.5, 10.2 | 0.063, 0.063, 0.069 |
| | 5 | 11.7, 11.7, 11.5 | 0.027, 0.027, 0.028 |
| Lavender | 1 | 1.49, 1.64, 1.64 | 0.052, 0.054, 0.054 |
| | 2 | 8.91, 9.21, 9.20 | 0.061, 0.059, 0.058 |
| | 3 | 11.0, 11.3, 11.3 | 0.044, 0.040, 0.041 |
| Eucalyptus | 1 | 1.64, 1.64, 1.49 | 0.054, 0.054, 0.053 |
| | 2 | 8.15, 8.15, 8.12 | 0.071, 0.071, 0.079 |
| Patchouli | 1 | 1.64, 1.64, 1.49 | 0.055, 0.055, 0.040 |
| | 2 | 12.9, 12.9, 12.7 | 0.025, 0.024, 0.026 |
| | 3 | 13.3, 13.3, 13.1 | 0.025, 0.024, 0.024 |
| | 4 | 14.2, 14.2, 14.1 | 0.026, 0.025, 0.028 |

### *7.5 Raw Data for PAH Analysis*

| Table 34: PAH Analysis | | | | |
|---|---|---|---|---|
| | **Helium** | | **Nitrogen** | |
| Peak # | $t_R$ (min) | Peak width (min) | $t_R$ (min) | Peak width (min) |
| 1 | 3.20 | 0.716 | 3.12 | 0.704 |
| 2 | 9.64 | 0.249 | 9.19 | 0.209 |
| 3 | 15.9 | 0.104 | 15.3 | 0.127 |
| 4 | 16.7 | 0.083 | 16.1 | 0.093 |
| 5 | 19.0 | 0.066 | 18.4 | 0.061 |
| 6 | 23.6 | 0.067 | 22.8 | 0.056 |
| 7 | 23.8 | 0.066 | 23.1 | 0.053 |
| 8 | 29.3 | 0.079 | 28.6 | 0.074 |
| 9 | 30.4 | 0.070 | 29.6 | 0.061 |
| 10 | 36.3 | 0.077 | 35.5 | 0.072 |
| 11 | 35.5 | 0.073 | 35.7 | 0.066 |
| 12 | 41.3 | 0.096 | 40.5 | 0.130 |
| 13 | 41.4 | 0.071 | 40.6 | 0.071 |
| 14 | 42.6 | 0.078 | 41.8 | 0.081 |
| 15 | 46.9 | 0.080 | 46.1 | 0.080 |
| 16 | 47.0 | 0.097 | 46.2 | 0.088 |
| 17 | 47.9 | 0.089 | 47.0 | 0.101 |